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Diverse Reaction Courses in the Controlled Carbometalation of Heterocumulenes with Zirconium–Diene Complexes and Molecular Structures of Carbon Dioxide, Isocyanate, and Ketene 1:1 and 1:2 Inserted Compounds

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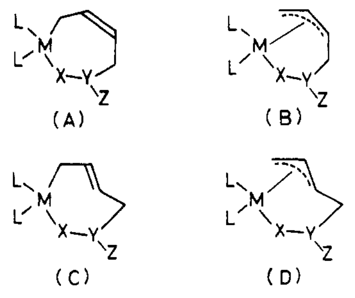
The carbometalation of various heterocumulenes (carbon dioxide, isocyanates, ketenes) was systematically investigated by using a series of zirconium–diene complexes of the type ZrL_2(*s-cis*-diene) and ZrL_2(*s-trans*-diene) (L = η^5-C_5H_5, η^5-C_5Me_5; diene = butadiene, isoprene) to clarify the essential factor(s) in determining the regio- and stereochemistry of the products. The mode of CO_2 insertion reaction changes drastically depending upon the bulkiness of the auxiliary ligand and the geometry (*s-cis*, *s-trans*) of ligated dienes. The 1:1 reactions of the ZrL_2(butadiene) complex with t-C_4H_9NCO, C_6H_5NCO, or $C_6H_5(CH_3)CCO$ yield Zr–O bound complexes having (σ,*syn*-η^3-allyl)metal structures, while the isoprene derivatives always give seven-membered-ring (*Z*)-oxametallacyclic isomers. The use of a bulky ketene, Ph_2CCO, resulted in an abnormal addition that provides a unique six-membered oxametallacycle. $(C_5Me_5)_2Zr[C_4H_6C(=O)O]$ belongs to the monoclinic space group $P2_1/n$ with a = 8.816 (1) Å, b = 28.916 (3) Å, c = 9.388 (1) Å, β = 108.89 (1)°, and Z = 4. $(C_5Me_5)_2Zr[C_4H_6C(=N$-t-$Bu)O]$ crystallizes in space group $Pbca$ with a = 14.458 (2) Å, b = 16.677 (3) Å, c = 22.446 (3) Å, and Z = 8. A 1:2 adduct, $(C_5Me_5)_2Zr[OC(=NC_6H_5)C_4H_6C(=NC_6H_5)O]$, crystallizes in space group $P2_12_12_1$ with a = 9.082 (2) Å, b = 17.275 (3) Å, c = 22.301 (4) Å, and Z = 4. The six-membered oxametallacycle $(C_5Me_5)_2Zr[CH{=}C(CH_3)CH(CH_3)C(=C(C_6H_5)_2)O]$ crystallizes in space group $P2_1/c$ with a = 12.282 (3) Å, b = 16.082 (3) Å, c = 17.981 (4) Å, β = 108.56 (3)°, and Z = 4. Thus, the configuration of the β-carbon (sp^2, sp^3) in the product together with the steric bulk of substituents on C(2) and/or C(3) of the ligated diene is found to be crucial in determining the reaction courses and the regio- and stereochemistry of the products.

Group 4A and group 5A early-transition-metal–diene complexes have received considerable current attention because of their unique M–C bonding properties (bent *s-cis* and novel *s-trans* coordination) and their high reactivities that have enabled a broad range of selective carbometalations to take place with both electrophiles (saturated and unsaturated aldehydes, ketones, esters, and nitriles) and unsaturated hydrocarbons (alkenes, dienes, alkynes).[2,3] Perhaps the most fascinating property of this class of diene complexes lies in their facile interconversions between σ^2,π-η^4-metallacyclo-3-pentene or π^2-η^4-*s-trans*-diene–metal species and transitory η^2-*s-cis*- or η^2-*s-trans*-metal–diene species generated during their versatile reactions.[2–7] This unusual behavior imparts a special utility to these diene complexes as a convenient means of revealing the chemical and structural features of early transition organometallics because the subtle differences existing in these complexes and substrates can be amplified effectively on the regio- and stereochemistry of the reaction products.

The current major problems are to find (1) the essential factor(s) in determining the structures of the final products, i.e. (*Z*)-metallacycle (A), (σ,*anti*-η^3-allyl)metal (B), (*E*)-metallacycle (C), or (σ,*syn*-η^3-allyl)metal species (D) for which the X, Y, and Z groups assume the sp^3 or sp^2 configuration, (2) factor(s) in controlling the reaction courses (single and double carbometalations), (3) a correlation between the geometry of the coordinated dienes (*s-cis* or *s-trans*) and the stereochemistry of the products, and (4) the effect of alkyl substitution at the diene ligand on the regiochemistry of the products.



X=O, N, CR, CHR
Y=C, CR, CRR′,
Z=O, OR, NR, NRR′, CRR′, CR$_3$

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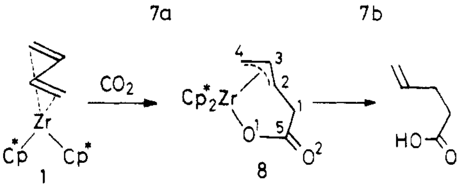
In order to solve these problems, we have examined carbometalations of heterocumulenes (carbon dioxide, isocyanates, ketenes),[8] which serve as bifunctional electrophiles, with an extended series of diene–zirconium complexes possessing either bulky C_5Me_5 or less bulky C_5H_5 (Cp) ligands together with a *s-cis-* or a *s-trans*-diene ligand. The molecular structures of the 1:1 adducts of $Zr(C_5Me_5)_2$(*s-trans*-butadiene) (**1**) with CO_2 and *t*-BuNCO, the 1:1 adduct of $Zr(C_5Me_5)_2$(*s-cis*-isoprene) (**2**) with $Ph_2C{=}C{=}O$, and the 1:2 adduct of $Zr(C_5Me_5)_2$(*s-trans*-butadiene) with PhN=C=O have been crystallographically characterized to obtain a sound experimental basis for the mechanistic considerations. Other zirconium–diene complexes studied here include $Zr(C_5H_5)_2$(*s-cis*-butadiene) (**3**), $Zr(C_5H_5)_2$(*s-cis*-isoprene) (**4**), $Zr(C_5H_5)_2$(*s-cis*-2,3-dimethylbutadiene) (**5**), and $Zr(C_5Me_5)_2$(*s-cis*-2,3-dimethylbutadiene) (**6**).

Results and Discussion

Reaction Courses for the Addition of Diene Complexes to Carbon Dioxide. Zirconium–diene complexes were found to readily react with carbon dioxide under atmospheric pressure in hydrocarbon solvents. The mode of insertion changes drastically depending upon the bulkiness of the ancillary ligand (C_5H_5 or C_5Me_5) along with the geometry (*s-cis* or *s-trans*) of the coordinated dienes. These reactions can be classified into three groups on the basis of the reaction stoichiometry (1:1, 1:2, or 2:1 ratio). The present experiments provide important information about the effects of the configuration (sp^2 or sp^3) of Y on the stereochemistry of the products.

(a) 1:1 Addition of ZrCp*$_2$(*s-trans*-butadiene) to CO_2. A *s-trans*-diene complex ligated by bulky Cp*-(C_5Me_5), i.e. ZrCp*$_2$(*s-trans*-butadiene) (**1**), readily reacts with CO_2 at 15 °C in benzene to yield solely the 1:1 adduct **8** of structure D in >95% yield, while a low-valent zirconium compound, $ZrCp_2(PMe_3)_2$, is reported to give a complexed polymeric product upon contact with CO_2.[9]

7a 7b



(1)

The addition of excess carbon dioxide to **1** or **8** did not induce the double insertion even at elevated temperatures (60–80 °C). The mass spectrum of the 1:1 adduct **8** reveals its monomeric nature. The ^{1}H NMR spectral data (see Tables III and IV) indicate that the butadiene moiety is bound to the metal in *syn*-η^3-allyl fashion as has been reported for $(PMe_3)_3Fe[CRCH{=}CHRCH_2C({=}O)O]$[10] and $LNi[CH_2C(CH_3)C(CH_3)CH_2C({=}O)O]$.[11] Similar metal–carbon framework has also been reported for $Cp_2Zr[C_4H_6C({=}Cr(CO)_5)O]$,[12a] $Cp_2Zr[C_4H_6C({=}CoCp(CO))O]$[12b] and $Cp_2Th[C_4H_6C({=}Cr(CO)_5O]$.[12c] The C–O stretching vibrations, 1660 cm^{-1} in IR and 1660 cm^{-1} in Raman, clearly confirm the ester-type linkage **7a** rather than the carboxylate structure **7b** where only one oxygen atom of the OC(O) group interacts with the metal. The ester-type bonding has already been reported for several titanium compounds like $Cp_2Ti[OC({=}O)C_6H_4C({=}O)O]$ (1665 cm^{-1}),[13] $Cp_2Ti[C_6H_4C({=}O)O]$ (1660 cm^{-1}),[14] Cp*$_2$$Ti[OC({=}O)CH_2CH_2]$ (1657 cm^{-1}),[15] and $Cp_2Ti[OC({=}O)\cdot PMe_3]$,[16] while low-valent titanium compounds, for example, Cp*$_2$Ti[OC(=O)R] (R = C_3H_5, C_4H_7; ca. 1535 cm^{-1}),[17] and a zirconium (IV) compound, $ZrClCp_2[OC({=}$

Table I. Interatomic Bond Distances (Å) and Angles (deg) for Non-Hydrogen Atoms in the ZrCp*$_2$(*s-trans*-butadiene)/CO_2 (1:1) Adduct (8) with Estimated Standard Deviations in Parentheses

(a) Bond Distances

Zr–O(1)	2.144 (4)	C(11)–C(12)	1.408 (8)
Zr–C(2)	2.709 (15)	C(11)–C(15)	1.427 (9)
Zr–C(3)	2.483 (14)	C(11)–C(16)	1.506 (10)
Zr–C(4)	2.403 (7)	C(12)–C(13)	1.394 (9)
Zr–C(11)	2.524 (6)	C(12)–C(17)	1.497 (10)
Zr–C(12)	2.592 (6)	C(13)–C(14)	1.443 (9)
Zr–C(13)	2.618 (6)	C(13)–C(18)	1.517 (11)
Zr–C(14)	2.571 (7)	C(14)–C(15)	1.404 (9)
Zr–C(15)	2.567 (6)	C(14)–C(19)	1.524 (11)
Zr–C(21)	2.559 (6)	C(15)–C(20)	1.508 (11)
Zr–C(22)	2.612 (7)	C(21)–C(22)	1.406 (9)
Zr–C(23)	2.581 (9)	C(21)–C(25)	1.425 (9)
Zr–C(24)	2.560 (7)	C(21)–C(26)	1.523 (10)
Zr–C(25)	2.576 (6)	C(22)–C(23)	1.419 (11)
O(1)–C(5)	1.299 (8)	C(22)–C(27)	1.472 (12)
O(2)–C(5)	1.212 (9)	C(23)–C(24)	1.421 (11)
C(2)–C(3)	1.187 (21)	C(23)–C(28)	1.479 (15)
C(3)–C(4)	1.436 (16)	C(24)–C(25)	1.415 (10)
C(1)–C(2)	1.465 (17)	C(24)–C(29)	1.497 (13)
C(1)–C(5)	1.539 (11)	C(25)–C(30)	1.505 (11)

(b) Bond Angles

O(1)–Zr–C(4)	121.2 (2)	C(13)–C(14)–C(19)	125.4 (6)
Zr–O(1)–C(5)	135.6 (4)	C(15)–C(14)–C(19)	126.0 (6)
Zr–C(2)–C(1)	110.4 (8)	C(11)–C(15)–C(14)	107.7 (5)
Zr–C(2)–C(3)	66.3 (10)	C(11)–C(15)–C(20)	125.9 (6)
C(2)–C(3)–C(4)	138.2 (14)	C(14)–C(15)–C(20)	123.4 (6)
Zr–C(4)–C(3)	76.0 (6)	C(22)–C(21)–C(25)	108.6 (5)
C(1)–C(2)–C(3)	138.8 (14)	C(22)–C(21)–C(26)	124.7 (6)
C(2)–C(1)–C(5)	111.3 (8)	C(25)–C(21)–C(23)	125.9 (6)
O(1)–C(5)–O(2)	123.7 (7)	C(21)–C(22)–C(23)	108.4 (6)
O(1)–C(5)–C(1)	115.5 (6)	C(21)–C(22)–C(27)	125.9 (6)
O(2)–C(5)–C(1)	120.7 (7)	C(23)–C(22)–C(27)	124.7 (7)
C(12)–C(11)–C(15)	107.8 (5)	C(22)–C(23)–C(24)	107.1 (7)
C(12)–C(11)–C(16)	126.0 (6)	C(22)–C(23)–C(28)	126.4 (8)
C(15)–C(11)–C(16)	125.6 (6)	C(24)–C(23)–C(28)	125.5 (8)
C(11)–C(12)–C(13)	109.1 (5)	C(23)–C(24)–C(25)	109.1 (6)
C(11)–C(12)–C(17)	124.7 (6)	C(23)–C(24)–C(29)	124.6 (7)
C(13)–C(12)–C(17)	126.0 (6)	C(25)–C(24)–C(29)	125.9 (7)
C(12)–C(13)–C(14)	107.4 (5)	C(21)–C(25)–C(24)	106.8 (6)
C(12)–C(13)–C(18)	126.4 (6)	C(21)–C(25)–C(30)	126.3 (6)
C(14)–C(13)–C(18)	124.7 (6)	C(24)–C(25)–C(30)	124.4 (6)
C(13)–C(14)–C(15)	107.8 (6)		

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Table II. Crystallographic and Experimental Data for 8, 23a, 24a, and 34

	8	23a	24a	34
formula	$C_{25}H_{36}O_2Zr$	$C_{29}H_{45}NOZr$	$C_{38}H_{46}N_2O_2Zr$	$C_{39}H_{48}OZr$
system	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	$P2_1/n$	*Pbca*	$P2_12_12_1$	$P2_1/c$
a, Å	8.816 (1)	14.458 (2)	9.082 (2)	12.282 (3)
b, Å	28.916 (3)	16.677 (3)	17.275 (3)	16.082 (3)
c, Å	9.388 (1)	22.446 (3)	22.301 (4)	17.981 (4)
β, deg	108.89 (1)			108.56 (3)
V, $Å^3$	2264.2 (5)	5411.9 (14)	3498.9 (13)	3367.1 (15)
Z	4	8	4	4
D_{calcd}, g cm^{-3}	1.348	1.264	1.241	1.231
F(000), e	904	2192	1376	1728
μ(Mo Kα), cm^{-1}	5.0	4.2	3.0	4.1
T, °C	20	20	20	20
2θ limits, deg	$4 < 2\theta < 55$	$4 < 2\theta < 55$	$4 < 2\theta < 50$	$4 < 2\theta < 55$
scan type	θ–2θ	θ–2θ	θ–2θ	θ–2θ
scan speed, deg min^{-1} in 2θ	4.0	4.0	4.0	4.0
scan width, deg in 2θ	2.0 + 0.70 tan θ	2.0 + 0.70 tan θ	2.0 + 0.70 tan θ	2.0 + 0.70 tan θ
bkgd counting, s	5	5	5	5
data collected	$+h,+k,\pm l$	$+h,+k,+l$	$+h,+k,+l$	$+h,+k,\pm l$
unique data	5202	6206	3478	7724
reflctns obsd	3851	3755	1831	5431
no. of params refined	398	470	178	563
goodness of fit	1.40	0.82	0.67	1.14
R(*F*)	0.060	0.076	0.131	0.066
$R_w(F)$	0.084	0.099	0.144	0.088

O)R] (1442–1528 cm^{-1}),[18] are known to prefer bonding of type **7b**. Comparison of these spectra reveals the 18e σ,η^3-*syn*-allyl structure **8** for the present 1:1 addition compound (eq 1). The fact that hydrolysis of **8** afforded 4-pentenoic acid supports this formulation. The *E* geometry for **8** contrasts sharply to that of aldehyde, ketone, ester, or acid amide inserted products of the *Z* geometry.[2] The marked difference may arise from the sp^2 configuration of the O(CO) carbon located at the β-position, which causes destabilization of the (*Z*)-oxametallacyclic conformation as a result of the high rigidity of the OC(=O)C group in addition to the relatively large O(1)–C(5)–C(1) angle, ϕ_1 (see Table VI).

The structural details of the CO_2 adduct were gained from an X-ray diffraction study of complex **8**. The molecular structure is given in Figure 1 along with the numbering scheme. A listing of the relevant bond distances and angles is given in Table I. Crystal data and parameters for the data collections and refinements are given in Table II. The zirconium atom is tetracoordinated if the Cp and allyl groups are each considered to occupy only one coordination site. The butadiene unit is bound to the metal in a twisted *syn*-η^3-allyl fashion. The torsional angle around the C(2)–C(3) bond (150.3°) thereby deviates largely from 180°. The OC(=O) group was found to assume the expected ester-type structure, where one oxygen atom, O(1), links to the metal while the other is bent away from the metal. The geometrical distortion around the *syn*-η^3-allyl group brings about substantial lengthening of the Zr–C(2) bond (2.709 Å) relative to the Zr–C(4) (2.403 Å) and Zr–C(3) (2.483 Å) bonds. The Zr–C(2) bond of this molecule is longer than the corresponding bond between Zr and terminal carbon of η^3-allyl groups (2.442–2.624 Å) in $ZrCp(\eta^3\text{-allyl})_2(\eta^1\text{-allyl})$.[19a] All of these Zr–C bonds are remarkably longer as expected than the Zr–C single bonds (2.21–2.27 Å) reported for $[ZrCp_2Me{\cdot}THF]^+$,[20] $ZrCp_2Me_2$,[21] $ZrCp_2(C_6H_4)$,[22] $ZrCp_2Cl(CH_2OCH_3)$,[19b] and $ZrCp_2(RC{\equiv}CH)$.[23] The Zr–O bond length (2.144 Å) is nearly comparable with those for $[Cp_2Zr(OCH_2CH_2CH_2)]_2$ (2.190 Å)[24] and $Cp_2Zr[OC(=M(CO)_5)CH_2CHCHCH_2]$ (M = Cr, 2.138 Å)[10] but longer than the Zr–O bonds (1.95–1.97 Å) in $[ZrCp_2O]_3$,[25] $ZrCp^*_2Cl(OH)$,[26a] and $ZrCp^*_2(OH)_2$.[26b] The C(5)–O(2) (1.212 Å) and C(5)–O(1) bonds (1.299 Å) exhibit normal lengths. The O(1)–C(5)–C(1) angle (115.5°) of **8** exceeds the angles of 106–107° found for ketone inserted oxametallacycles,[2d] reflecting the sp^2 configuration of the C(5) carbon in **8**. Although the $CH_2CHCHCH_2CO_2$ group in **8** interacts with the metal at both of its ends, O(1), O(2), C(5), and C(1) atoms show almost no perturbation from coplanarity (the dihedral angle between the O(1)–C(5)–O(2) and O(2)–C(5)–C(1) planes is only 0.6°); i.e. the C(5) carbon has a strain-free sp^2 configuration. The σ,*syn*-η^3-allyl-type coordination of the diene unit causes an expansion of O(1)–Zr–C(4) angle to 121.2° from those (89–90°) for ketone-inserted (*Z*)-oxazirconacyclo-4-heptenes.[2d] The whole geometry of the present CO_2 adduct resembles well those for iron and nickel derivatives $(PR_3)_3Fe[C_5H_8C(=O)O]$[10] and $(TMEDA)Ni[CH_2C(CH_3)C(CH_3)CH_2C(=O)O]$.[11]

(b) 1:2 Addition of *s-cis*-Diene Complexes of $Zr(C_5Me_5)_2$ to CO_2. Zirconium complexes bearing both *s-cis*-coordinated dienes and bulky ancillary ligands, i.e., $ZrCp^*_2$(*s-cis*-isoprene) (**2**) and $ZrCp^*_2$(*s-cis*-2,3-dimethylbutadiene) (**6**), readily undergo the double insertion of CO_2 at 20 °C in benzene. The formation of the 1:1 adduct **9** or **10**, which corresponds to **8**, is undetectable even when 1 equiv of carbon dioxide is slowly added to **2** or **6** at low temperatures. The resulting crystalline product assumes

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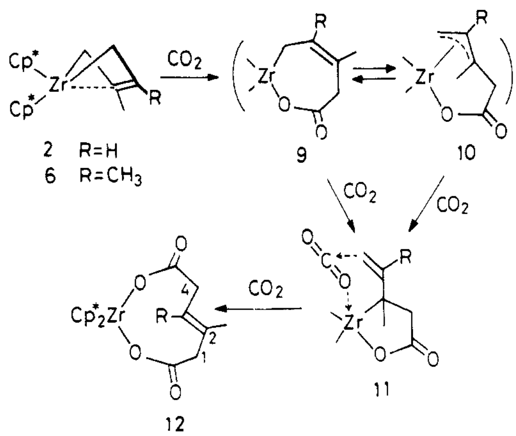
the 1,3-dioxazircona-6-nonene structure (12) (see eq 2) as

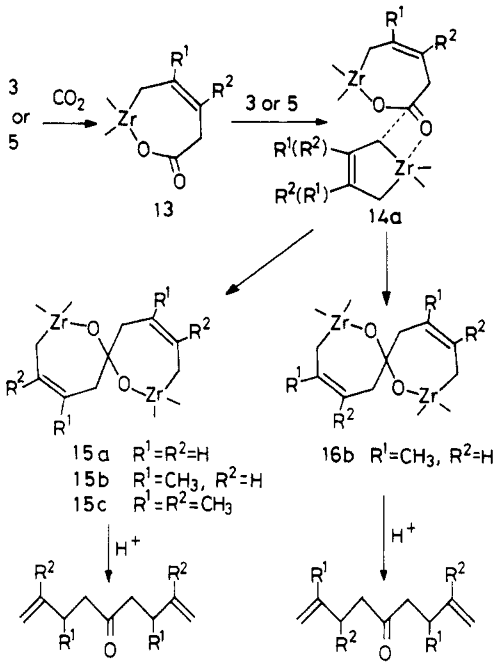


(2)

supported by EIMS and NMR spectroscopies together with elemental analyses. Hydrolysis of **12** afforded the desired dicarboxylic acid in good yield. The marked difference of the *s-trans* complex **1** and the *s-cis* complex **3** observed in the modes of their reactions may be rationalized in the following manner. In the first step of the addition reaction, carbon dioxide should attack the C(1) carbon of the coordinated isoprene to generate the 16e transient (*Z*)-oxazirconacycle **9**, the regio- and stereochemistry of which is essentially the same as those found for the insertion reactions of ketones with Zr–diene complexes.[2] The presence of a methyl group at the γ-position of **9** may be the major factor preventing the formation of an 18e (σ,*syn*-η^3-allyl)metal complex of type **10**, due to the severe steric repulsion between the isoprene methyl and Cp* groups. Since the presumed adduct **9** is an electron-deficient species and exhibits severe ring strain as a result of the planar OC(O) group, the addition of excess CO_2 should force the species **9** to react further, presumably via an intermediate **11**, to give the geometrically and thermodynamically more stable adduct **12** having *E* geometry. A similar intermediate has been proposed for the 1:2 addition of $ZrCp_2(C_4H_6)$ to acetone, which led to a (*E*)-1,3-dioxazirconacyclo-6-nonene.[2a,b,g]

(c) 2:1 Addition of $ZrCp_2$(diene) to CO_2. The mode of the CO_2 insertion varies greatly when the less bulky Cp was used in place of the bulky Cp* ligand, regardless of the geometry and the bulkiness of ligated dienes. Treatment of $ZrCp_2$(*s-cis*-butadiene) (**3**) with excess carbon dioxide (1 atm) in benzene at ambient temperature was found to provide a novel binuclear oxazirconium compound (**15**) containing a spiro-type bicyclic skeleton (eq 3). This formulation is consistent with EIMS and NMR data. Carbonyl stretching vibrations are absent in their IR spectra in the region 1400–1800 cm^{-1} in support of the spiro-type linkage. The hydrolysis of **15a** gave the desired dibutyl ketones (nonadien-5-one) in ca. 80% yield; i.e., hydrolysis of **15a** in ether gave primarily 1,8-nonadien-5-one (80% selectivity) while the hydrolysis in hexane prefers the formation of 1,7-nonadien-5-one (70%) and 2,7-nonadien-5-one (30%).

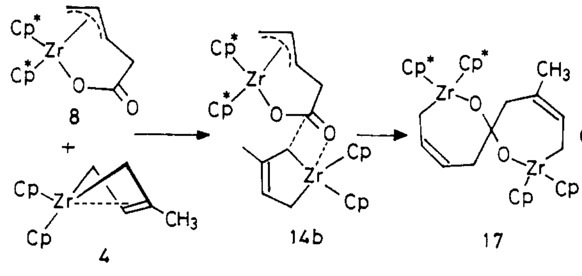
Similarly, $ZrCp_2$(*s-cis*-isoprene) (**4**) and $ZrCp_2$(*s-cis*-2,3-dimethylbutadiene) (**5**) were converted into analogous spiro compounds **15b**/**16b** and **15c**, respectively, via **14a** by treating them with excess carbon dioxide (1 atm). The resulting 2:1 adducts **15b** and **16b** yield a mixture of 3,7-dimethyl-1,8-, 3,7-dimethyl-1,7-, 3,7-dimethyl-2,7-, and 2,7-dimethyl-1,7-nonadien-5-one in a 9:28:30:33 ratio on hydrolysis (see eq 3). This means that carbon dioxide preferentially attacks the C(1) carbon of the coordinated isoprene with 85% regioselectivity in good accord with the



(3)

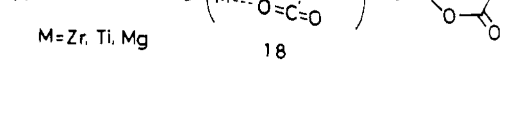
regiochemistry reported for the addition reactions of **4** with carbonyl compounds.[2]

In order to clarify the reaction pathway for the present unique 2:1 addition reaction, a model reaction was examined by using **8** and $ZrCp_2$(*s-cis*-isoprene) (**4**). An intermolecular reaction occurred smoothly, presumably via intermediate **14b**, and gave the desired spiro-type oxazirconacyclic compound **17** which gives upon hydrolysis a mixture of 3-methyl-1,8-nonadien-5-one and 3-methyl-1,7-nonadien-5-one in a 5:95 ratio (eq 4). Thus, this sequence provides good experimental support for the reaction pathway illustrated in eq 3. A similar acetal linkage (i.e. $ZrOCR_2OZr$) has been postulated as an intermediate in the thermolysis of $ZrCp_2Cl[O(CO)R]$ leading to $(ZrCp_2Cl)_2O$.[18] More remarkable is the fact that the above reaction sequences bring about a geometrical change of the butadiene unit from *E* to *Z*. This change may be correlated directly to the configurational change of the O(CO) sp^2 carbon in **8** to a sp^3 carbon (acetal carbon) during the reaction; i.e., the placement of sp^3 carbon at the β-position brings about the (*Z*)-oxametallacyclic structure while that of sp^2 carbon gives rise to the *E* structure.



(4)

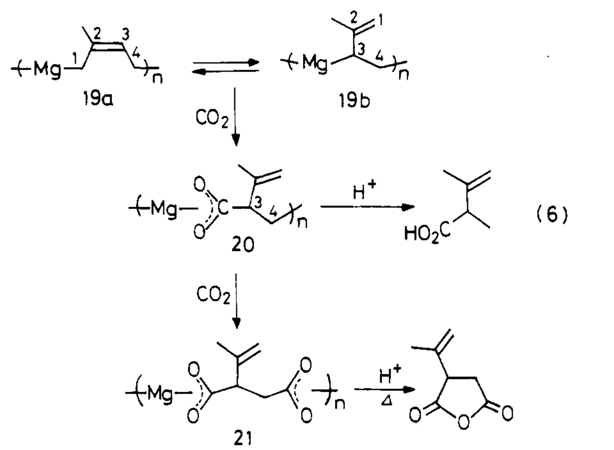
(d) Addition of Acyclic Allylmetal Compounds to CO_2. The mode of CO_2 insertion with allylic metal compounds such as $ZrCp_2(\eta^1$-2-butenyl$)_2$ and $TiCp_2(\eta^3$-2-butenyl) differs greatly from those mentioned above. In these cases, CO_2 adds to the γ-carbon and the product gives upon hydrolysis 2-methyl-3-butenoic acid. A six-membered transition state, shown in eq 5, seems most likely for these



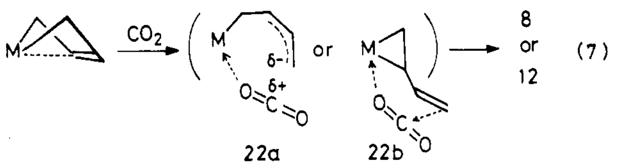
(5)

reactions since the regiochemistry is essentially the same as those reported for the insertion reactions of carbonyl compounds into allylic metal compounds.[27]

The mode of reaction in the carboxylation of (2-methyl-2-butene-1,4-diyl)magnesium (**19**)[28] with carbon dioxide also differs distinctly from those with zirconium–diene complexes. The addition of 0.5–0.8 equiv of CO_2 to **20** in THF resulted in the predominant attack of CO_2 to the isoprene C(3) atom to give the adduct **20**, which yields upon hydrolysis 2,3-dimethyl-3-butenoic acid in good yield. Further addition of carbon dioxide affords the dicarboxylate **21** as a consequence of the subsequent attack of carbon dioxide to the isoprene C(4) carbon (eq 6).

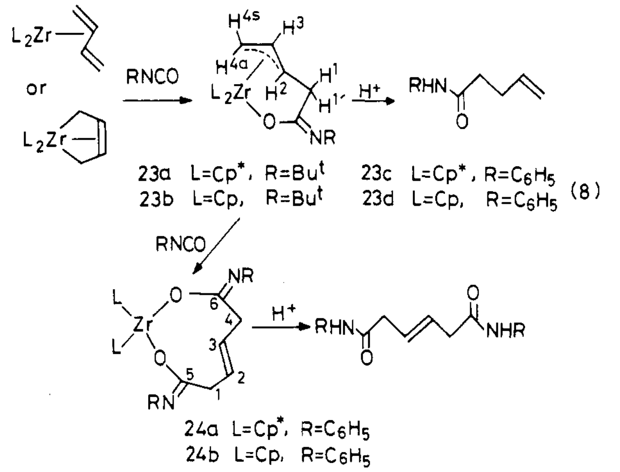


Hydrolysis followed by distillation of the product in vacuo gave isoprenylsuccinic acid anhydride in good yield as a result of thermal dehydration of the dicarboxylic acid during distillation. Thus, noncyclic metal–diene compounds behave as conventional allylmetal compounds. With reference to the mode of the above reactions, we can propose a reaction pathway involving either transition state **22a** or **22b** for the carboxylation of zirconium–diene complexes with CO_2. The coordination geometries of these intermediates satisfy the molecular orbital requirements inherent in the Cp_2M fragment.[29]



Reaction Courses for the Addition of Diene Complexes to Isocyanates. Reactions of alkyl or phenyl isocyanate with a series of zirconium–diene complexes have been explored in order to find what differences, if any, might be observed relative to the isoelectronic CO_2 reactions.

(a) Addition Reactions of *s-cis*- and *s-trans*-Zr(C_5R_5)$_2$(butadiene) to Isocyanates. Alkyl isocyanates typified by *t*-BuNCO readily undergo the 1:1 addition reaction with ZrCp*$_2$(*s-trans*-butadiene) (**1**) on treating them in benzene at ambient temperatures (eq 8). The



whole geometry of the product compares very closely to that of the CO_2-inserted compound **8** as deduced from NMR studies.

It is important to point out that both the *s-trans*-butadiene complex (**1**) and the *s-cis*-butadiene complex (**3**) produce only the 1:1 adduct of σ,*syn*-η^3-allyl)metal structure on their reactions with *t*-BuNCO, whereas **3** gives only the 2:1 adduct with CO_2. The insertion of *t*-BuNCO at the CO, rather than the C=N-*t*-Bu, site is evident from the IR spectra. The adducts **23a** and **23b** (in hexane) display C=N stretching vibrations at 1610 and 1620 cm^{-1}, respectively. The above structural inference was finally confirmed by an X-ray analysis of **23a** (vide infra). A similar addition of phenyl isocyanate at its CO site has already been postulated for the addition reaction of $TiCp_2$(allyl) with PhNCO to give a 15e product[17] while $ZrCp_2Me_2$ is known to yield 16e $ZrCp_2Me[\eta^3$-OC(Me)NPh] in which both O and N atoms interact with metal.[30] Therefore we can presume that the 18e structures of the complexes **23** along with the steric bulk around the N atom are the major reasons why the C=NR group does not form the spiro-type linkage.

Thus, *t*-BuNCO-inserted *butadiene* complexes always assume the (σ,*syn*-η^3-allyl)metal structure (D) regardless of the initial geometry of the coordinated dienes (*s-cis* or *s-trans*) or the bulk of the ancillary ligands (Cp*, Cp), while the isoprene complexes form the geometrical isomer B exclusively, as described later.

^{1}H NMR chemical shifts and coupling constants for the isocyanate inserted products are listed in Tables III and IV, respectively. The (σ,*syn*-η^3-allyl)metal structure of the $L_2Zr[C_4H_6C(=NR)O]$ (L = Cp, Cp*) obtained from **1** (*s-trans* conformer) and **3** (*s-cis* conformer) is apparent from these data, which compare very closely with those for the CO_2-inserted compound **8**. When these data are compared with those of conventional (π-allyl)zirconium compounds, one can observe a large chemical shift difference between their terminal methylene protons. The methylene protons (H^{4a},H^{4s}) in **23a** and **23b** (1.41–184 ppm) show upfield shifts as compared with those for Zr(η^3-C_3H_5)$_4$[31] and Zr(C_8H_8)(*anti*-η^3,*anti*-η^3-C_8H_{12}).[32a] This is indicative of pronounced σ-bonding character at the metal–C(4) linkages in **23a** and **23b**. Furthermore, the chemical shifts for H(2) and H(3) clearly confirm the substantial olefinic character

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Table III. ^{1}H NMR Chemical Shift Values (δ, ppm) for the 1:1 Adduct of Diene Complexes with Heterocumulenes and Related Complexes Assuming a (σ,η^3-Allyl)metal or Metallacyclic Structure[a]

1:1 adduct	ν_{4a}	ν_{4s}	ν_3	ν_2	ν_1	$\nu_{1'}$	$\nu_{Cp(Cp^*)}$
$ZrCp^*_2$(*s-trans*-BD)/CO_2 (**8**)	1.38	1.57	4.54	3.61	3.10	2.63	1.65
							1.64
$ZrCp^*_2$(*s-trans*-BD)/*t*-BuNCO (**23a**)	1.41	1.52	4.69	3.92	3.51	2.81	1.70
							1.68
$ZrCp^*_2$(*s-trans*-BD)/PhNCO (**23c**)	1.82	1.98	4.83	4.04	3.49	2.90	1.64
							1.54
$ZrCp_2$(*s-cis*-BD)/*t*-BuNCO (**23b**)	1.71	1.84	5.07	4.54	3.33	2.47	5.44
							5.48
$ZrCp_2$(*s-cis*-BD)/PhNCO (**23d**)	1.86	2.04	5.00	4.35	3.38	2.55	5.50
							5.55
$ZrCp^*_2$(*s-cis*-IP)/*t*-BuNCO (**25a**)	3.14		6.03		2.02		1.82
$ZrCp_2$(*s-cis*-IP)/*t*-BuNCO (**25b**)	2.57		5.07		1.66		5.72
$ZrCp^*_2$(*s-trans*-BD)/PhMeCCO (**29**)	1.24	1.52	5.03	4.27	3.02	2.69	1.66
$ZrCp^*_2$(*s-cis*-IP)/PhMeCCO (**30**)	3.10		6.22		2.12		1.84
$ZrCp_2$(*s-cis*-BD)/$Cr(CO)_6$[b]	1.49	1.50	4.91	4.53	4.20	2.66	5.26
							5.23
$ThCp^*_2$(*s-cis*-BD)/$Cr(CO)_6$[c]	1.84	1.95	5.24	3.86	4.52	3.17	1.80
							1.78
$Zr(C_3H_5)_4$[d]	1.90	3.28	5.18		1.90	3.28	
$Zr(C_8H_8)(\eta^3,\eta^3\text{-}C_8H_{12})$[e]	3.75	3.38	6.39	1.91	2.30	1.42	

[a] Data were collected at 500 MHz in C_6D_6 at 30 °C and were analyzed by computer simulation. Abbreviations: BD, butadiene; IP, isoprene. [b] Reference 25. [c] Reference 12a. [d] Reference 32. [e] Reference 33. Numbering system is given in eq 1 and 8–10.

Table IV. Coupling Constants (Hz) for the 1:1 Adducts of Diene Complexes with Heterocumulenes and Related Complexes[a]

1:1 adduct	$J_{4a,4s}$	$J_{3,4a}$	$J_{3,4s}$	$J_{2,3}$	$J_{1,2}$	$J_{1',2}$	$J_{1,1'}$
$ZrCp^*_2$(*s-trans*-BD)/CO_2 (**8**)	-4.4	14.0	7.9	15.4	5.4	11.0	-16.1
$ZrCp^*_2$(*s-trans*-BD)/*t*-BuNCO (**23a**)	-4.1	13.1	7.6	15.0	4.9	11.0	-14.6
$ZrCp^*_2$(*s-trans*-BD)/PhNCO (**23c**)	-4.0	14.4	7.9	15.1	5.6	10.4	-14.6
$ZrCp_2$(*s*-Cis-BD)/*t*-BuNCO (**23b**)	-4.1	14.7	8.0	15.0	4.9	11.5	-15.4
$ZrCp_2$(*s-cis*-BD)/PhNCO (**23d**)	-4.0	13.2	7.8	15.2	5.0	11.0	-15.0
$ZrCp^*_2$(*s-cis*-IP)/*t*-BuNCO (**25a**)	?	7.6	7.6				?
$ZrCp_2$(*s-cis*-IP)/*t*-BuNCO (**25b**)	?	7.6	7.6				?
$ZrCp^*_2$(*s-trans*-BD)/PhMeCCO (**29**)	-4.2	14.2	8.2	15.4	5.0	11.0	-15.6
$ZrCp^*_2$(*s-cis*-IP)/PhMeCCO (**30**)	?	7.5	7.5				?
$ZrCp_2$(*s-cis*-BD)/$Cr(CO)_6$[b]	-4.0	13.5	8.4	15.9	4.7	9.8	-17.4
$ThCp^*_2$(*s-cis*-BD)/$Cr(CO)_6$[c]	-18.6	14.2	8.2	16.1	4.2	10.0	?
$Zr(C_3H_5)_4$[d]	0.5	15.5	8.5				
$Zr(C_8H_8)(\eta^3,\eta^3\text{-}C_8H_{12})$[e]		17.5	10.2	10.8			

[a] See Table II for data collections. [b–e] See references given in Table III.

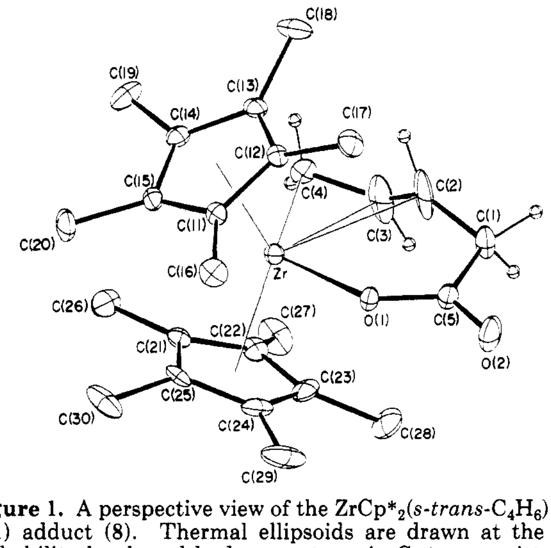


Figure 1. A perspective view of the $ZrCp^*_2(s\text{-}trans\text{-}C_4H_6)/CO_2$ (1:1) adduct (**8**). Thermal ellipsoids are drawn at the 20% probability level, and hydrogen atoms in Cp* are omitted for clarity.

of the C(2)–C(3) bond, leading to (*E*)-oxametallacyclo-4-heptene character for these complexes. Such chemical shift variations are also more or less observed when the molecule involves the σ,*syn*-η^3-allylmetal framework, e.g. $Cp_2Zr[C_4H_6C(=Cr(CO)_5)O]$,[10] $Cp_2Zr[CH_2CH_2CH_2CH=CHCH_2)]$,[3] etc.

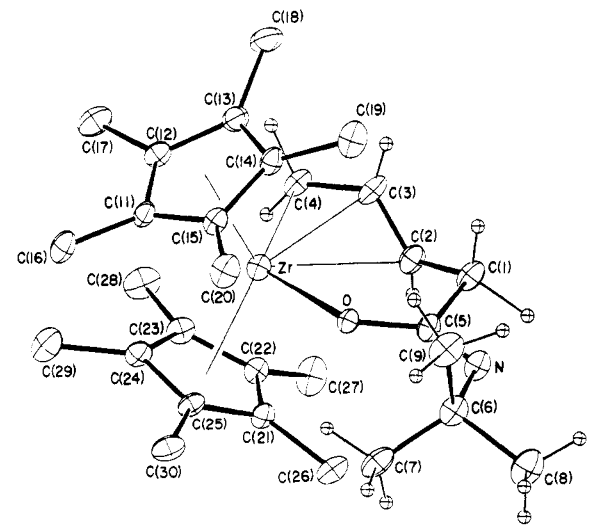


Figure 2. An ORTEP diagram and numbering scheme of the $ZrCp^*_2(s\text{-}trans\text{-}C_4H_6)/t\text{-}BuNCO$ (1:1) adduct (**23a**) showing 20% probability thermal ellipsoids. Hydrogen atoms in Cp* are omitted for clarity.

The exact molecular structure of the 1:1 adduct of isocyanate was finally obtained by the X-ray analysis of the $ZrCp^*_2$(*s-trans*-butadiene)/*t*-BuNCO adduct (**23a**). Its ORTEP drawing is illustrated in Figure 2 with the numbering scheme. Pertinent bond distances and angles are

Table V. Interatomic Bond Distances (Å) and Angles (deg) for Non-Hydrogen Atoms in the $ZrCp^*_2$(*s-trans*-C_4H_6)/*t*-BuNCO (1:1) Adduct (23a) with Estimated Standard Deviations in Parentheses

(a) Bond Distances

Zr-O	2.157 (5)	C(6)-C(8)	1.572 (14)
Zr-C(2)	2.671 (10)	C(6)-C(9)	1.540 (14)
Zr-C(3)	2.515 (9)	C(11)-C(12)	1.434 (12)
Zr-C(4)	2.420 (9)	C(11)-C(15)	1.398 (11)
Zr-C(11)	2.618 (8)	C(11)-C(16)	1.507 (13)
Zr-C(12)	2.577 (9)	C(12)-C(13)	1.421 (12)
Zr-C(13)	2.614 (9)	C(12)-C(17)	1.532 (13)
Zr-C(14)	2.574 (8)	C(13)-C(14)	1.411 (12)
Zr-C(15)	2.567 (8)	C(13)-C(18)	1.516 (14)
Zr-C(21)	2.602 (8)	C(14)-C(15)	1.437 (11)
Zr-C(22)	2.659 (7)	C(14)-C(19)	1.523 (13)
Zr-C(23)	2.625 (8)	C(15)-C(20)	1.501 (13)
Zr-C(24)	2.591 (8)	C(21)-C(22)	1.395 (11)
Zr-C(25)	2.525 (8)	C(21)-C(25)	1.411 (11)
O-C(5)	1.321 (9)	C(21)-C(26)	1.514 (12)
N-C(5)	1.279 (11)	C(22)-C(23)	1.407 (11)
N-C(6)	1.463 (11)	C(22)-C(27)	1.517 (13)
C(5)-C(1)	1.553 (13)	C(23)-C(24)	1.423 (11)
C(1)-C(2)	1.486 (14)	C(23)-C(28)	1.534 (14)
C(2)-C(3)	1.332 (13)	C(24)-C(25)	1.427 (11)
C(3)-C(4)	1.449 (13)	C(24)-C(29)	1.523 (12)
C(6)-C(7)	1.530 (13)	C(25)-C(30)	1.530 (12)

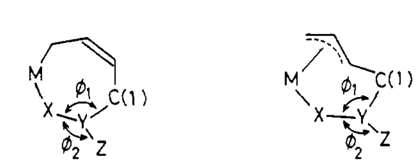
(b) Bond Angles

O-Zr-C(4)	121.8 (3)	C(12)-C(13)-C(14)	107.2 (7)
Zr-O-C(5)	134.3 (5)	C(12)-C(13)-C(18)	126.4 (8)
C(5)-N-C(6)	125.4 (7)	C(14)-C(13)-C(18)	125.2 (8)
O-C(5)-N	130.9 (8)	C(13)-C(14)-C(15)	109.0 (7)
O-C(5)-C(1)	114.4 (7)	C(13)-C(14)-C(19)	125.5 (8)
N-C(5)-C(1)	114.6 (7)	C(15)-C(14)-C(19)	125.1 (8)
C(5)-C(1)-C(2)	109.4 (8)	C(11)-C(15)-C(14)	107.2 (7)
Zr-C(2)-C(1)	110.6 (6)	C(11)-C(15)-C(20)	126.0 (8)
Zr-C(2)-C(3)	68.7 (6)	C(14)-C(15)-C(20)	125.8 (8)
C(1)-C(2)-C(3)	125.6 (9)	C(22)-C(21)-C(25)	108.4 (7)
C(2)-C(3)-C(4)	123.8 (9)	C(22)-C(21)-C(26)	125.8 (7)
Zr-C(4)-C(3)	76.6 (5)	C(25)-C(21)-C(26)	125.7 (7)
N-C(6)-C(7)	117.1 (7)	C(21)-C(22)-C(23)	108.9 (7)
N-C(6)-C(8)	105.1 (7)	C(21)-C(22)-C(27)	126.3 (7)
N-C(6)-C(9)	107.5 (7)	C(23)-C(22)-C(27)	123.7 (7)
C(7)-C(6)-C(8)	107.0 (7)	C(22)-C(23)-C(24)	107.6 (7)
C(7)-C(6)-C(9)	110.7 (8)	C(22)-C(23)-C(28)	127.6 (8)
C(8)-C(6)-C(9)	109.2 (8)	C(24)-C(23)-C(28)	123.8 (8)
C(12)-C(11)-C(15)	108.5 (7)	C(23)-C(24)-C(25)	107.3 (7)
C(12)-C(11)-C(16)	125.4 (8)	C(23)-C(24)-C(29)	123.0 (7)
C(15)-C(11)-C(16)	124.1 (8)	C(25)-C(24)-C(29)	127.5 (7)
C(11)-C(12)-C(13)	107.9 (7)	C(21)-C(25)-C(24)	107.6 (7)
C(11)-C(12)-C(17)	126.9 (8)	C(21)-C(25)-C(30)	126.3 (7)
C(13)-C(12)-C(17)	124.2 (8)	C(24)-C(25)-C(30)	125.4 (7)

listed in Table V. The molecule is best described as pseudotetrahedral about the metal with the twisted *syn*-η^3-allyl unit occupying one of the tetrahedral coordination sites. The *t*-BuNCO molecule has been inserted into the Zr–C(1) bond at its CO moiety, and the N-*t*-Bu group is bent away from the metal. Thus the whole geometry of **23a** is compatible with that of the CO_2-inserted complex **8**.

The most striking structural feature of **23a** emerges in the C(3)–C(4) and Zr–C(4) bonds. The C(3)–C(4) bond (1.449 Å) is the longest among the (η^3-allyl)zirconium family (Table VI) while the C(2)–C(3) bond distance (1.332 Å) is among the shortest. The Zr–C(4) bond (2.420 Å) is shorter while the Zr–C(2) bond (2.671 Å) is longer than those of typical (η^3-allyl)zirconium complexes.[31–33] These results indicate a substantial participation of the limiting (*E*)-oxazirconacyclo-4-heptene structure (C) in **23a** rather than the limiting (σ,η^3-allyl)zirconium form (D) as defined earlier. The deviation of C(1), C(2), C(3), and C(4) from the planar trans structure makes the torsional angle around the C(2)–C(3) bond, 158.9°, a little larger than the corresponding angle for **8** (150.3°).

The angle O–C(5)–C(1) of **23a**, ϕ_1 defined by X–Y–C(1) in C or D, almost equals that (115.5°) of the CO_2-inserted compound **8** (Table VI) but is remarkably larger than the ϕ_1 values (106.3–109.2°) for ketone-inserted oxametallacycles of geometry A reflecting the sp^2 configuration of the Y carbon for the former and the sp^3 configuration for the latter. The angle ϕ_2 defined by X–Y–Z, the sp^2 carbon bonded angle O(1)–C(5)–N for **23a** and O(1)–C(5)–O(2) for **8**, also exceed the sp^3 carbon bonded angles (106–110°) as found for ketone inserted compound.[2d] The deviation of the O, C(5), N, and C(1) atoms from coplanarity leads to a dihedral angle between the O–C(5)–N and C(5)–N–C(1) planes of 4.7°, indicating the presence of only a small ring strain in this fragment. These results inform us that the magnitude of the angle ϕ_1 serves as a crucial factor in determining the gross geometry of the final products, or D, when X is an oxygen atom. However, replacement of the oxygen atom at X with a CH_2, CHR, or CR= group invariably leads to complexes of structure D, regardless of the configuration (sp^2 or sp^3) of the X group.[2f,3c] This is due to the lengthening of the Zr–X single bond along with increased Lewis acidity of the Zr–C bonded complexes.



(A) (D)

Phenyl isocyanate has increased electrophilicity as compared with *t*-BuNCO, and hence this molecule can take part in both single and double insertions into $ZrCp^*_2$(*s-trans*-butadiene) (**1**) and $ZrCp_2$(*s-cis*-butadiene) (**3**). The 1:1 addition gives **23c** or **23d** of σ,*syn*-η^3-allyl structure while the 1:2 addition leads to nine-membered 1,3-dioxametallacycles **24a** and **24b** of *E* geometry (see Table VII). Acid cleavage of **24a** and **24b** gave the expected (*E*)-dicarboxylic acid amides quantitatively (see eq 8).

The X-ray analysis of adduct **24a**, $Cp^*_2Zr[OC(=NC_6H_5)C_4H_6C(=NC_6H_5)O]$, was also undertaken to obtain unambiguous evidence regarding the macrocyclic structure of the doubly inserted isocyanate compounds. The gross geometry of **24a** is depicted in Figure 3 along

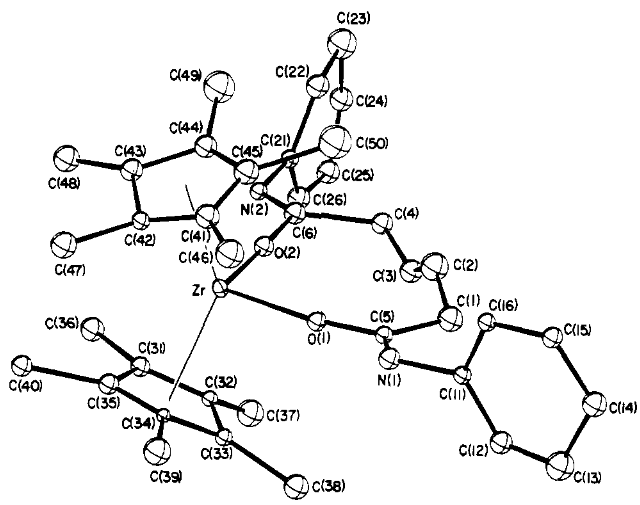


Figure 3. A perspective view of the $ZrCp^*_2$(*s-trans*-C_4H_6)/C_6H_5NCO (1:2) adduct (**24a**) showing 10% probability thermal ellipsoids.

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Table VI. Summary of Zr–C and C–C Bond Distances (Å) and Angles of X–Y–C(1) (ϕ_1) and X–Y–Z (ϕ_2) for the 1:1 Adducts of Zirconium–Diene and Related Complexes

complexes	confor-matn[a]	Zr–C(4)	Zr–C(3)	Zr–C(2)	C(3)–C(4)	C(2)–C(3)	ϕ_1	ϕ_2	ref
$Cp^*_2Zr[CH_2CH{=}CHCH_2C({=}O)O]$ (**8**)	D	2.403	2.483	(2.709)	1.436	(1.187)	115.5	123.7	this work
$Cp^*_2Zr[CH_2CH{=}CHCH_2C({=}N\text{-}t\text{-}Bu)O]$ (**23a**)	D	2.420	2.575	2.671	1.499	1.332	114.4	130.9	this work
$Cp_2Zr[CH_2CH{=}CHCH_2C({=}CoCp(CO))O]$	D	2.423	2.492	2.614	1.403	1.304	111.5	122.0	11
$Cp_2Zr(CH_2CH{=}CHCH_2CH_2CH_2)$	D	2.461	2.481	2.641	*b*	*b*	*b*	*b*	3
$Cp_2Zr[CH_2C(CH_3){=}CHCH_2C(CH_3){=}C(CH_3)]$[c]	D	2.427	2.595	2.522	1.421	1.361	124.5	118.4	40a
$(C_8H_8)Zr(CH_2CH{=}CHCH_2CH_2CH{=}CHCH_2)$		2.823 2.826	2.529 2.534	2.379 2.391	1.360 1.362	1.446 1.439			32a
$Cp^*_2Zr[CH_2CH{=}CHCH_2C(i\text{-}C_3H_7)_2O]$	A	2.294	3.144	3.702	1.482	1.313	106.6	106.7 110.0	2d
$Cp^*_2Zr[CH_2CH{=}C(CH_3)CH_2C(i\text{-}C_3H_7)_2O]$[c]	A	2.311	3.177	3.729	1.494	1.324	106.3	106.6 109.0	2d
$Cp_2Zr[CH_2CH{=}CHCH_2C(C_6H_5)_2O]$	A	2.311	3.051	3.612	1.468	1.351	107.2	110.1 107.7	3

[a] Conformations are given in the Introduction. [b] Atomic coordinates are not given. [c] Numbering system is as follows: C(4), allyl terminal; C(3), $C(CH_3)$ carbon; C(2), isoprene C(3) carbon.

Table VII. ^{1}H NMR Parameters for the 1:2 Adducts of Diene Complexes with Heterocumulenes Involving 1,3-Dioxametallacyclo-6-nonene or 1,3-Dioxametallacycloheptane Structure[a]

1:2 adduct	chemical shift values (δ, ppm)				coupling constants (Hz)						
	$\nu_{4,4'}$	ν_3	ν_2	$\nu_{1,1'}$	$J_{4,4'}$	$J_{3,4}$	$J_{3,4'}$	$J_{2,3}$	$J_{1,2}$	$J_{1',2}$	$J_{1,1'}$
$ZrCp^*_2$(*s-cis*-IP)/$2CO_2$ (**12**)	3.17	5.11		3.07	?	7.8	7.8				?
$ZrCp^*_2$(*s-trans*–BD)/2PhNCO (**24a**)	2.79, 3.02	5.14	5.14	2.79, 3.02	−8.0	7.0	7.3	15.1	7.0	7.3	−8.2
$ZrCp_2$(*s-cis*-BD)/2PhNCO (**24b**)	2.75, 2.98	5.03	5.03	2.75, 2.98	−8.0	7.0	7.4	15.0	7.0	7.4	−8.0
$ZrCp^*_2$(*s-cis*-IP)/2PhNCO (**28a**)	2.98	5.08		2.88	?	8.0	8.0				?
$ZrCp_2$(*s-cis*-BD)/$2(CH_3)_2CO$	1.18, 2.14	5.37	5.37	1.18, 2.14	−8.0	7.0	7.3	15.2	7.0	7.3	−8.0
$ZrCp_2$(*s-cis*-BD)/2PhMeCCO (**31a**)	2.51, 2.66	5.02	5.02	2.51, 2.66	−8.2	7.1	7.3	15.0	7.1	7.3	−8.2
$ZrCp_2$(*s-cis*-IP)/2PhMeCCO (**31b**)	2.77	4.98		2.65	?	7.8	7.8				?
$ZrCp_2$(*s-cis*-BD)/$2Ph_2CCO$ (**39a**)	2.84, 3.16	3.67	6.46	5.05, 5.18	−14.8	2.0	7.8	7.0	16.7	10.0	−13.2
$ZrCp_2$(*s-cis*-IP)/$2Ph_2CCO$ (**39b**)	2.72, 2.97	3.70		4.77, 4.93	14.1	2.9	8.8				−13.0

[a] Data were collected at 100 MHz in C_6D_6 at 30 °C and analyzed by computer simulation. Numbering system follows those given in eq 2 and 9–12. Abbreviations: BD, butadiene; IP, isoprene.

with the numbering scheme (full lists of bond distances and angles are given in supplementary material). The total accuracy of the molecular structure is severely affected by the low quality of the X-ray data, especially at the higher diffraction angles. However, the ORTEP plot clearly confirms the nine-membered 1,3-dioxazircona-6-nonene structure and the *E* geometry of the olefinic C(2)–C(3) bond. Each of the two phenyl isocyanate molecules is bound through carbon to one opposite end of the butadiene unit and is bound to the metal through its oxygen atom. The whole molecule has an approximate twofold symmetry passing through the C(2)–C(3) bond and Zr atom. The torsional angle around the C(2)–C(3) bond is 161°, deviating significantly from 180°. Seven of the atoms involved in the nine-membered ring are lie in a plane to within 0.06 Å, while the other two atoms, C(2) and C(3), deviate from coplanarity by 0.17 and 0.30 Å, respectively, on opposite sides. This is the first X-ray structure of such nine-membered early-transition-metal compounds. In the case of related 12-membered-ring macrocyclic titanium compounds, $[TiCp_2OC(O)CR{=}CRC(O)O]_2$, both planar and nonplanar conformations have been reported.[34] The Zr–O bond distances (2.00 (2) and 2.01 (2) Å) and the angles around the isocyanate, O(1)–C(5)–N(1) = 115 (3)°, O(2)–C(6)–N(2) = 125 (4)°, C(5)–N(1)–C(11) = 121 (3)°, and C(6)–N(2)–C(21) = 123 (3)°, are all reasonable. The O(1)–Zr–O(2) bite angle (98.7 (8)°) in **24a** is significantly larger than the O–Zr–C angles for seven-membered oxazirconacycles (89.6–91.9°) and those for six-membered oxazirconacycles like $ZrCp_2(OCH_2CH_2SiMe_2CH_2)$ (91.0°),[35a] $ZrCp_2[OC({=}CH_2)SiMe_2CO({=}CH_2)]$ (89.7°),[35b] and $ZrCp^*_2[O(CH_2)_4]$ (84.1°).[35c] We must refrain from further description of structural details because of the insufficient positional accuracy of the diene carbon atoms.

(b) Addition of *s-cis*-Zr(C_5R_5)(isoprene) to Isocyanates. The products from the *isoprene* complexes differ drastically from those obtained from butadiene complexes in regards to their geometry. The reaction of *tert*-butyl isocyanate with $ZrCp_2$(*s-cis*-isoprene) (**4**) or $ZrCp^*_2$(*s-cis*-isoprene) (**2**) provides a high yield (97–100%) of the 1:1 product **25** having the (*Z*)-oxametallacyclic structure (A), not the (σ,*syn*-η^3-allyl)metal structure (D), irrespective of the bulkiness of the auxiliary ligand (eq 9). This marked difference may originate from the higher conformational stability of the *Z* structure as a consequence of the severe steric repulsions between the isoprene methyl group and the Cp rings expected for the *E* isomer, C or D.

The NMR patterns of the isoprene derivatives **25a** and **25b** differ significantly from those of **23a** and **23b** having the σ,*syn*-η^3-allyl structure derived from *s-cis*- and *s-trans*-butadiene complexes (Table III). The downfield shift of the isoprene methylene protons (H^{4a}, H^{4s}) is ascribable to the (*Z*)-oxametallacyclic structure. However, the chemical shift values of H^{4a} and H^{4s} (2.6–3.1 ppm) are

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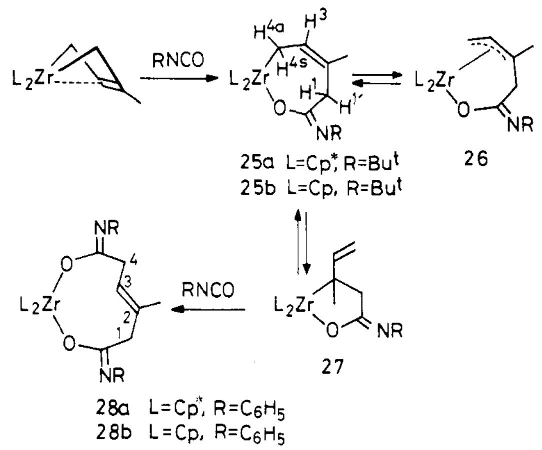
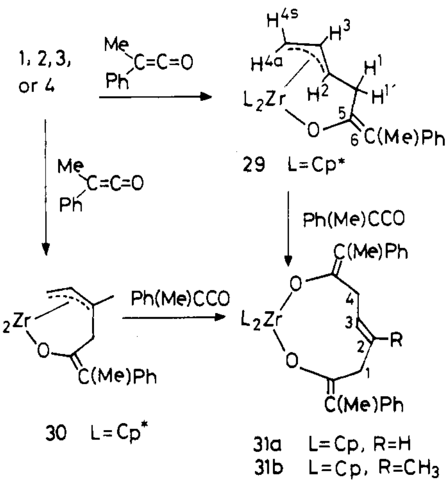


(9)

much larger when compared with those (1.4–1.7 ppm) for a typical structurally well-defined (*Z*)-oxametallacycle, $Cp^*{}_2\overline{Zr[C_5H_8C(i\text{-}C_3H_7)_2O]}$, indicating that the ($\sigma$,*anti*-$\eta^3$-allyl)metal bonding character (**26**) is quite pronounced in the present complexes.

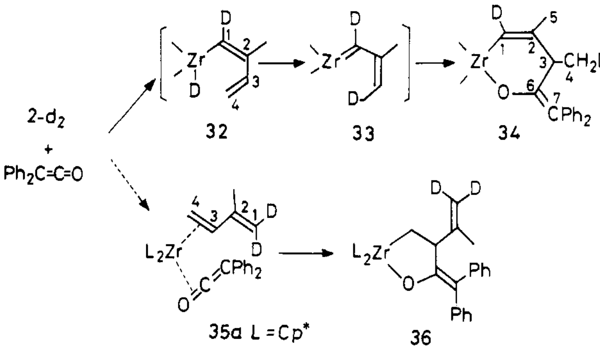
Subsequent addition of *t*-BuNCO to the resultant compounds **25a** and **25b** did not induce a double insertion even when the mixture was heated to 80 °C in toluene. By contrast, phenyl isocyanate can undergo the double insertion under mild conditions (30 °C for 12 h) even when only 1 equiv of PhNCO was added to **2** or **4**. That the ensuing 1:2 adducts **28a,b** have *E* geometry was confirmed by ^{1}H NMR together with differential NOE measurement (Table VII). Thus, the reaction pathway through **27** is reasonably proposed as suggested also by the double insertion of CO_2 (see eq 2).

Addition of $Zr(C_5R_5)_2$(diene) to Ketenes. (a) Addition of Zirconium–Diene Complexes to Methylphenylketene. Substituted and nonsubstituted ketenes (ethenone) are highly polarized as $R_2C^-{=}C^+{=}O^-$ and generally undergo [2 + 2] and/or [2 + 4] cycloadditions spontaneously with alkenes, alkynes, dienes, and saturated or α,β-unsaturated carbonyl compounds.[36] If these characteristics contribute in reactions with zirconium–diene complexes, they may give rise to new types of metallacycloaddition reactions. To address this possibility we have carried out reactions between methylphenylketene (3-phenylpropenone) and several zirconium–diene complexes. The addition of $ZrCp^*{}_2(C_4H_6)$ (**1**) to $C_6H_5(CH_3)$-C=C=O resulted in a high yield (97–99%) of the normal σ,η^3-allyl-bonded 1:1 adduct (**29**) possessing *E* geometry while $ZrCp^*{}_2(C_5H_8)$ (**2**) affords a metallacyclic compound, **30**, having *Z* geometry (eq 10) as revealed by the ^{1}H NMR studies (Tables III and IV). The preferential reaction at the C=O site has also been reported for the ketene complexes of early transition metals,[37] while Pt–ketene complexes usually undergo the reaction at the ketene C–C site.[38] When the complexes with the less bulky Cp ligand (**3** and **4**) were used, the double insertion of methylphenylketene proceeds smoothly at 0 °C to yield the 1:2 adducts **31a** and **31b**, respectively. Thus, we can conclude that methylphenylketene displays essentially the same regio- and stereochemistry as observed in the phenyl isocyanate insertion reactions.



(10)

(b) Abnormal Addition by Diphenylketene. A bulky ketene, diphenylketene, was found to undergo a fundamentally different type of cycloaddition reaction. Surprisingly, the stoichiometric addition of $ZrCp^*{}_2$(isoprene) (**1**) to diphenylketene provides a novel six-membered oxametallacycle (**34**) as the sole observable product in 95% yield (eq 11) whose structure was established by the X-ray



(11)

analysis. Note that the C(3) carbon of the isoprene ligand is bound to the central carbon atom of the ketene in this case. A possible reaction pathway is given in eq 11, with support from labeling experiments involving $ZrCp_2$-$[CD_2{=}C(CH_3)CH{=}CH_2]$ (**2**-d_2). One of the deuterium atoms at the C(1) position of the isoprene-d_2 migrated onto the C(4) position during the metallacyclization as evidenced by the ^{1}H NMR studies; i.e., the quartet of the methine proton at C(3) changes to a triplet and the singlet assigned to C(1) proton disappears as a result of the deuterium labeling. Deuterium scrambling to other positions is negligible. The severe steric repulsion between the Cp* methyls and the isoprene methyl together with the steric repulsion between the ketene phenyls and the isoprene molecule should prevent a normal insertion but allow for a very unusual α-elimination at the electron-rich CD_2 terminus in **2**-d_2. The rearrangement of the metal deuteride, leading to a novel vinyl carbene complex, **33**, followed by the successive [2 + 4]-type coupling may eventually afford **34**. A related agostic interaction has been reported between Ti and the α-CH_2 group in $TiCp^*$-$(CH_2Ph)_3$[39] and between Ti and Me in sterically congested octahedral methyltitanium compounds as predicted from

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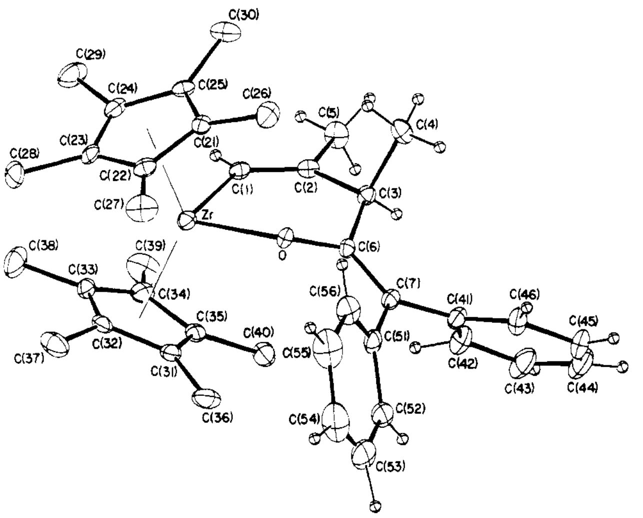

Figure 4. An ORTEP diagram of the $ZrCp_2$(*s-cis*-isoprene)/diphenylketene (1:1) adduct (**34**). Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms in Cp* are omitted for clarity.

an EHMO calculation.[40] The tautomerism between alkenylmetal (**32**) and metal–carbene (**33**) forms has also been postulated in the conversion of $HfCp_2(CH_2C_6H_5)_2$ to a hafnacycle[41] and in the formation of $ZrCp^*_2Cl(CH{=}CMe)ZrClCp_2$.[42] Several zirconium carbenes have recently been isolated owing to their stabilization through phosphine coordination.[43] The location of the metal center in a steric pocket should prevent the normal cyclic addition leading to **36** through **35a**. Further details of deuterium migration remain equivocal. In contrast to the present case, diphenylketene has been reported to undergo the normal addition to $ZrCp_2Me_2$, which produces $ZrCp_2Me(OCMe{=}CPh_2)$ or $ZrCp_2(OCMe{=}CPh_2)_2$.[30]

The X-ray structural studies on the diphenylketene inserted complex **34** provide clear evidence for the six-membered oxametallacyclic framework as illustrated in Figure 4. Table VIII contains selected bond distances and angles for the non-hydrogen atoms of **34**. It is obvious from the ORTEP drawing that the diphenylketene is bound to the metal through its oxygen atom and bound to the C(3) carbon atom of the isoprene unit at its central carbon, C(6). Consequently the molecule contains a six-membered ring. The molecule involves olefinic bonds at the C(1)–C(2) and the C(6)–C(7) positions, and hence the Zr, C(1), C(2), C(3), C(5), and H(1) atoms as well as the O, C(6), C(7), and C(3) atoms are both nearly coplanar. A dihedral angle of 29.1° is formed between these two planes. The O–C(6) bond distance (1.345 Å) is a little shorter than a typical C–O single bond. The bond angles around the C(3) atom indicate the normal sp^3 configuration. The bite angle (82.3°) defined by O–Zr–C(1) is slightly smaller than that of ketone-inserted seven-membered oxametallacycles (90–92°, vide supra), reflecting the smaller ring size of **34**, but larger than that of five-membered oxametallacycle (72.2°).[24]

Abnormal C–C bond formation is also found in the double insertion of diphenylketene into $ZrCp_2(C_4H_6)$ (**3**) and $ZrCp_2(C_5H_8)$ (**4**) to give **38**, where the ketene is bound to C(3) of the isoprene or C(2) of the butadiene unit, respectively. Since the 1:1 reaction of **5** with diphenylketene produces a complex formulated as **37** (a common structure with **36**) as detected by the low-temperature ^1H NMR spectroscopy, we can postulate that the double insertion follows the course indicated by eq 12. The regiochemistry involved in this process is entirely different from that postulated for thermally induced 1:1 and 1:2 insertions of simple ketones and aldehydes.

However, the regiochemistry observed for **38** is in accord with those for the addition product from zirconium–diene complexes and unsaturated hydrocarbons (1-alkenes, alkynes, and conjugated dienes),[2,3,44] as well as the products

Table VIII. Interatomic Bond Distances (Å) and Angles (deg) for Non-Hydrogen Atoms in the $ZrCp^*_2$(*s-trans*-butadiene)/Diphenylketene (1:1) Adduct (34) with Estimated Standard Deviations in Parentheses

(a) Bond Distances

Zr–O	2.000 (4)	C(23)–C(28)	1.532 (11)
Zr–C(1)	2.236 (6)	C(24)–C(25)	1.408 (9)
Zr–C(21)	2.561 (6)	C(24)–C(29)	1.535 (11)
Zr–C(22)	2.531 (6)	C(25)–C(30)	1.515 (10)
Zr–C(23)	2.579 (7)	C(31)–C(32)	1.437 (9)
Zr–C(24)	2.564 (6)	C(31)–C(35)	1.410 (8)
Zr–C(25)	2.581 (6)	C(31)–C(36)	1.504 (10)
Zr–C(31)	2.533 (6)	C(32)–C(33)	1.408 (9)
Zr–C(32)	2.555 (6)	C(32)–C(37)	1.495 (11)
Zr–C(33)	2.605 (6)	C(33)–C(34)	1.397 (9)
Zr–C(34)	2.596 (6)	C(33)–C(38)	1.512 (13)
Zr–C(35)	2.551 (6)	C(34)–C(35)	1.420 (9)
C(1)–C(2)	1.344 (8)	C(34)–C(39)	1.505 (11)
C(2)–C(3)	1.530 (8)	C(35)–C(40)	1.522 (10)
C(2)–C(5)	1.529 (9)	(C41)–C(42)	1.405 (10)
C(3)–C(4)	1.553 (9)	C(41)–C(46)	1.411 (10)
C(3)–C(6)	1.511 (8)	C(42)–C(43)	1.414 (12)
C(6)–C(7)	1.364 (8)	C(43)–C(44)	1.366 (14)
O–C(6)	1.345 (6)	C(44)–C(45)	1.365 (14)
C(7)–C(41)	1.485 (9)	C(45)–C746)	1.424 (13)
C(7)–C(51)	1.484 (9)	C(51)–C(52)	1.402 (12)
C(21)–C(22)	1.422 (8)	C(51)–C(53)	1.389 (10)
C(21)–C(25)	1.397 (8)	C(52)–C(53)	1.394 (18)
C(21)–C(26)	1.512 (10)	C(53)–C(54)	1.380 (22)
C(22)–C(23)	1.429 (9)	C(54)–C(55)	1.409 (19)
C(22)–C(27)	1.493 (11)	C(55)–C(56)	1.402 (13)
C(23)–C(24)	1.396 (9)		

(b) Bond Angles

O–Zr–C(1)	82.3 (2)	C(32)–C(31)–C(35)	107.3 (5)
Zr–O–C(6)	138.0 (3)	C(32)–C(31)–C(36)	124.7 (6)
Zr–C(1)–C(2)	126.4 (4)	C(35)–C(31)–C(36)	127.9 (6)
C(1)–C(2)–C(3)	127.3 (5)	C(31)–C(32)–C(33)	107.5 (5)
C(1)–C(2)–C(5)	120.5 (5)	C(31)–C(32)–C(37)	123.0 (6)
C(3)–C(2)–C(5)	112.1 (5)	C(33)–C(32)–C(37)	128.2 (6)
C(2)–C(3)–C(4)	109.0 (5)	C(32)–C(33)–C(34)	109.0 (6)
C(2)–C(3)–C(6)	117.6 (5)	C(32)–C(33)–C(38)	126.5 (7)
C(4)–C(3)–C(6)	108.6 (5)	C(34)–C(33)–C(38)	123.4 (7)
O–C(6)–C(3)	114.9 (5)	C(33)–C(34)–C(35)	107.9 (6)
O–C(6)–C(7)	120.5 (5)	C(33)–C(34)–C(39)	126.3 (6)
C(3)–C(6)–C(7)	124.3 (5)	C(35)–C(34)–C(39)	125.1 (6)
C(22)–C(21)–C(25)	109.0 (5)	C(31)–C(35)–C(34)	108.3 (5)
C(22)–C(21)–C(26)	124.2 (5)	C(31)–C(35)–C(40)	126.3 (6)
C(25)–C(21)–C(26)	126.5 (6)	C(34)–C(35)–C(40)	125.3 (6)
C(21)–C(22)–C(23)	106.4 (5)	C(42)–C(41)–C(46)	117.6 (6)
C(21)–C(22)–C(27)	124.9 (6)	C(41)–C(42)–C(43)	121.6 (7)
C(23)–C(22)–C(27)	127.9 (6)	C(42)–C(43)–C(44)	118.8 (8)
C(22)–C(23)–C(24)	107.9 (6)	C(43)–C(44)–C(45)	122.2 (9)
C(22)–C(23)–C(28)	124.1 (6)	C(44)–C(45)–C(46)	119.8 (9)
C(24)–C(23)–C(28)	126.7 (6)	C(41)–C(46)–C(45)	120.0 (7)
C(23)–C(24)–C(25)	109.0 (6)	C(52)–C(51)–C(56)	118.7 (7)
C(23)–C(24)–C(29)	125.9 (6)	C(51)–C(51)–C(53)	119.9 (9)
C(25)–C(24)–C(29)	124.5 (6)	C(52)–C(53)–C54)	119.8 (13)
C(21)–C(25)–C(24)	107.5 (5)	C(53)–C(54)–C(55)	122.3 (14)
C(21)–C(25)–C(30)	126.2 (6)	C(54)–C(55)–C(56)	116.2 (10)
C(24)–C(25)–C(30)	125.8 (6)	C(51)–C(56)–C(55)	122.9 (8)

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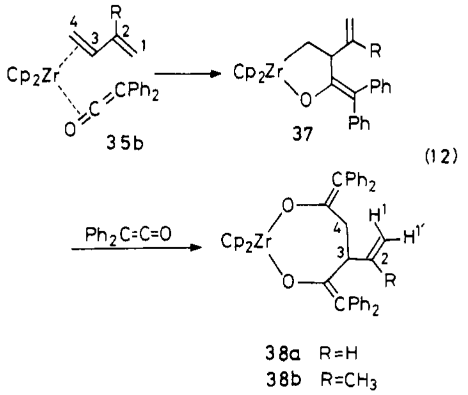
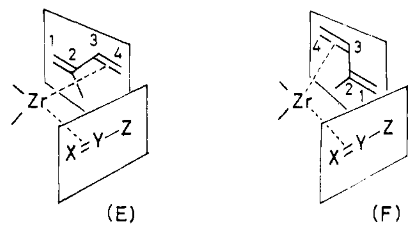


from the photoinduced addition of **3** to carbonyl compounds.[3] Therefore, a pathway through **35b** is proposed for the present reaction. The unusual regiochemistry for these reactions can be rationalized by the steric repulsion between Cp, the isoprene methyl, and the ketene phenyl groups. In general, two coordination geometries, E and F, are plausible for the oxidative coupling. Electrophiles usually take part in C–C bond formation through species E, but the present reaction indicates that the addition through species F becomes favorable when the bulky diphenylketene is employed. The concomitant generation of regioisomers through the species corresponding to E and F has been reported for the isoprene–isoprene,[2a,e] allene–allene,[45] and diene–alkyne[2e,44] couplings on the MCp_2 (M = Ti, Zr) sphere, while CO_2–CO_2[16] and ketene–ketene couplings[46] give only one isomer. Refer also the theoretical studies on the bis(olefin)–metallacyclopentane interconversion.[47]



Concluding Remarks

The carbometalation of heterocumulenes (CO_2, isocyanates, ketenes) with zirconium–diene complexes was found to give either a σ,*syn*-η^3-allyl- or a σ,*anti*-η^3-allyl-type 1:1 adduct depending upon the steric bulk of the ligated dienes and auxiliary ligand (Cp* or Cp), while simple ketones, aldehydes, and esters always provide (*Z*)-oxametallacyclo-3-pentene derivatives, regardless of the geometry of the ligated dienes (*s-trans*, *s-cis*) or the steric bulk of the diene and Cp ligands. The configuration of the β-carbon atoms (sp^2 or sp^3) in the ensuing 1:1 adduct is concluded to be the key factor in determining the geometry. Double carbometalation is also possible when the oxazirconacycle possesses a hydrogen atom on its δ-carbon, although alkyl substitution on that carbon always hampers the double carbometalation.[2g] Although various selective reactions with organotitanium compounds have been known,[48] the present studies were found to offer more general guidelines on the regio- and stereochemistry along with the reaction courses since the corresponding diene complexes of Ti,[49a] Hf,[49a] Ta,[49b,c] and Nb[49d] also undergo the same type of reactions. Such versatile and highly selective addition reactions under mild conditions have never been found for the middle- and late-transition-metal complexes, and one can readily envision a whole body of applications for the present chemistry in organic synthesis.

Table IX. Fractional Atomic Coordinates and B_{eq} for $Cp^*_2Zr[C_4H_6C(=O)O]$ (8)

atom	x	y	z	B_{eq}, Å^2
Zr	0.26404 (6)	0.376030 (16)	0.30637 (5)	2.33
O(1)	0.2319 (5)	0.30466 (14)	0.2418 (5)	2.6
O(2)	0.2701 (7)	0.23493 (18)	0.1619 (18)	5.4
C(1)	0.4973 (9)	0.2855 (3)	0.2420 (10)	4.3
C(2)	0.5361 (10)	0.3299 (4)	0.3205 (16)	8.0
C(3)	0.5391 (10)	0.3698 (4)	0.2909 (16)	7.3
C(4)	0.5187 (8)	0.4137 (3)	0.3539 (8)	3.2
C(5)	0.3203 (8)	0.2726 (3)	0.2117 (8)	3.2
C(11)	0.1297 (7)	0.3491 (3)	0.4918 (7)	2.6
C(12)	0.2875 (7)	0.3325 (2)	0.5539 (6)	2.5
C(13)	0.3918 (7)	0.3699 (3)	0.5992 (6)	3.0
C(14)	0.2963 (8)	0.4115 (3)	0.5657 (7)	2.9
C(15)	0.1348 (8)	0.3983 (3)	0.5056 (7)	2.7
C(16)	−0.0201 (8)	0.3201 (3)	0.4417 (9)	3.8
C(17)	0.3321 (9)	0.2825 (3)	0.5790 (8)	4.0
C(18)	0.5661 (9)	0.3678 (4)	0.6979 (8)	5.1
C(19)	0.3581 (11)	0.4602 (3)	0.6127 (9)	4.7
C(20)	−0.0028 (10)	0.4290 (3)	0.5074 (9)	4.8
C(21)	0.1304 (7)	0.4455 (2)	0.1455 (7)	2.6
C(22)	0.2295 (8)	0.4271 (3)	0.0684 (7)	3.1
C(23)	0.1732 (10)	0.3822 (3)	0.0167 (7)	3.9
C(24)	0.0331 (9)	0.3743 (3)	0.0566 (7)	3.8
C(25)	0.0041 (7)	0.4135 (3)	0.1344 (7)	2.8
C(26)	0.1408 (10)	0.4948 (3)	0.2051 (8)	4.4
C(27)	0.3498 (11)	0.4529 (4)	0.0224 (11)	5.6
C(28)	0.2294 (14)	0.3528 (4)	−0.0852 (9)	6.9
C(29)	−0.0753 (12)	0.3334 (3)	0.0078 (11)	7.3
C(30)	−0.1545 (9)	0.4244 (4)	0.1552 (10)	5.5

Experimental Section

General Remarks. All manipulations were conducted under dry argon by using standard Schlenk techniques. Tetrahydrofuran, benzene, toluene, and hexane were dried over Na/K alloy and thoroughly purged of molecular oxygen by trap-to-trap distillation before use. Pure samples of zirconium–diene complexes were prepared according to the method described previously.[2c,d] ^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 (high resolution) and a JEOL Model O1SG-2 spectrometer (low resolution), where organometallics were transferred into the inlet under argon atmosphere. Elemental analysis, gas chromatographic analysis, and melting point measurement were conducted as described before.[2c–e]

Structure Determination of 8, 23a, 24a, and 34. A single crystal of **8**, **23a**, **24a**, and **34** sealed in a thin-walled glass capillary under argon was mounted on a Rigaku automated four-circle diffractometer. Relevant crystal and data statics are summarized in Table II. The unit cell parameters at 20 °C were determined by a least-squares fit to 2θ values of 25 (for **8**, **23a**, and **24a**) and 40 (for **34**) strong higher angle reflections. Each sample showed no significant intensity decay during the data collection. The crystal structures of the above complexes were all solved by the

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Table X. Fractional Atomic Coordinates and B_{eq} for $Cp^*_2Zr[C_4H_6C(=N\text{-}t\text{-}Bu)O]$ (23a)

atom	x	y	z	B_{eq}, Å^2
Zr	0.07922 (5)	0.18401 (4)	0.15106 (3)	3.31
O	0.1481 (4)	0.1262 (3)	0.0774 (2)	2.7
N	0.2008 (5)	0.0204 (4)	0.0161 (3)	3.8
C(1)	0.0839 (8)	−0.0070 (6)	0.0884 (4)	4.0
C(2)	0.0579 (7)	0.0250 (6)	0.1479 (5)	3.8
C(3)	−0.0214 (7)	0.0617 (6)	0.1610 (4)	4.0
C(4)	−0.0334 (7)	0.1143 (6)	0.2118 (4)	3.9
C(5)	0.1529 (6)	0.0515 (5)	0.0580 (4)	3.4
C(6)	0.2626 (7)	0.0643 (6)	−0.0239 (4)	4.1
C(7)	0.3241 (7)	0.1287 (6)	0.0041 (4)	4.8
C(8)	0.3288 (8)	−0.0012 (7)	−0.0508 (5)	5.9
C(9)	0.2030 (8)	0.1001 (7)	−0.0741 (5)	5.4
C(11)	0.0349 (6)	0.3268 (5)	0.1120 (4)	3.3
C(12)	−0.0418 (6)	0.2972 (5)	0.1460 (4)	3.6
C(13)	−0.0825 (6)	0.2330 (5)	0.1137 (4)	3.8
C(14)	−0.0271 (6)	0.2197 (5)	0.0630 (4)	3.4
C(15)	0.0470 (6)	0.2772 (5)	0.0624 (4)	3.2
C(16)	0.0778 (7)	0.4087 (5)	0.1184 (5)	4.7
C(17)	−0.0853 (7)	0.3364 (6)	0.2010 (5)	4.9
C(18)	−0.1778 (7)	0.1977 (6)	0.1238 (6)	5.3
C(19)	−0.0486 (8)	0.1609 (6)	0.0129 (4)	4.8
C(20)	0.1133 (7)	0.2912 (6)	0.0120 (5)	4.7
C(21)	0.2404 (6)	0.1518 (5)	0.1967 (4)	3.1
C(22)	0.1798 (6)	0.1359 (5)	0.2436 (3)	3.1
C(23)	0.1363 (6)	0.2078 (5)	0.2607 (4)	3.6
C(24)	0.1740 (6)	0.2705 (5)	0.2251 (4)	3.4
C(25)	0.2360 (6)	0.2344 (5)	0.1835 (4)	3.2
C(26)	0.3044 (7)	0.0916 (6)	0.1675 (4)	4.3
C(27)	0.1745 (8)	0.0589 (6)	0.2794 (4)	5.2
C(28)	0.0743 (7)	0.2222 (7)	0.3150 (5)	5.3
C(29)	0.1676 (7)	0.3587 (6)	0.2421 (5)	5.1
C(30)	0.2979 (7)	0.2798 (6)	0.1396 (4)	4.5

Table XI. Fractional Atomic Coordinates and B for $Cp^*_2Zr[OC(=NC_6H_5)C_4H_6C(=NC_6H_5)O]$ (24a)

atom	x	y	z	B_{eq} (B), Å^2
Zr	0.0950 (3)	0.17137 (16)	0.21129 (11)	3.2[a]
O(1)	0.156 (3)	0.0821 (12)	0.1597 (9)	3.5
O(2)	0.143 (3)	0.2581 (12)	0.1544 (10)	4.1
N(1)	0.214 (4)	−0.0372 (16)	0.1416 (12)	4.3
N(2)	0.159 (3)	0.3827 (14)	0.1261 (11)	3.1
C(1)	0.258 (5)	0.056 (3)	0.0644 (17)	5.0
C(2)	0.279 (6)	0.144 (3)	0.059 (3)	8.6
C(3)	0.227 (5)	0.207 (3)	0.0488 (17)	5.5
C(4)	0.248 (5)	0.284 (3)	0.0563 (18)	6.0
C(5)	0.211 (4)	0.0313 (17)	0.1227 (13)	2.6
C(6)	0.181 (4)	0.320 (3)	0.1163 (15)	5.2
C(11)	0.273 (4)	−0.1024 (18)	0.1035 (14)	4.0
C(12)	0.190 (5)	−0.133 (3)	0.0563 (16)	5.0
C(13)	0.224 (6)	−0.194 (3)	0.028 (3)	8.6
C(14)	0.400 (6)	−0.223 (3)	0.0420 (17)	6.7
C(15)	0.469 (4)	−0.189 (2)	0.0883 (14)	4.6
C(16)	0.414 (4)	−0.1300 (16)	0.1204 (12)	3.4
C(21)	0.195 (4)	0.4415 (19)	0.0866 (14)	3.6
C(22)	0.341 (5)	0.468 (3)	0.0861 (17)	6.1
C(23)	0.384 (7)	0.539 (3)	0.050 (3)	9.7
C(24)	0.254 (5)	0.563 (3)	0.0143 (17)	5.3
C(25)	0.129 (4)	0.537 (2)	0.0060 (15)	4.8
C(26)	0.108 (5)	0.4749 (19)	0.0477 (14)	4.7
C(31)	−0.155 (4)	0.2368 (17)	0.2110 (17)	4.0
C(32)	−0.145 (3)	0.1980 (16)	0.1593 (12)	2.5
C(33)	−0.157 (4)	0.1216 (18)	0.1664 (13)	2.8
C(34)	−0.147 (3)	0.1088 (16)	0.2306 (11)	2.4
C(35)	−0.161 (4)	0.170 (3)	0.2605 (13)	4.1
C(36)	−0.172 (4)	0.320 (3)	0.2275 (16)	6.2
C(37)	−0.185 (6)	0.240 (3)	0.103 (3)	8.4
C(38)	−0.162 (5)	0.060 (3)	0.1132 (19)	7.1
C(39)	−0.159 (6)	0.021 (4)	0.256 (3)	9.8
C(40)	−0.204 (5)	0.188 (3)	0.3276 (16)	5.8
C(41)	0.272 (5)	0.109 (3)	0.2811 (18)	5.3
C(42)	0.189 (4)	0.1483 (16)	0.3156 (13)	3.3
C(43)	0.220 (5)	0.239 (2)	0.3024 (16)	5.1
C(44)	0.326 (5)	0.227 (3)	0.2579 (16)	5.0
C(45)	0.348 (5)	0.153 (3)	0.2496 (19)	6.4
C(46)	0.282 (6)	0.023 (3)	0.283 (3)	8.6
C(47)	0.107 (7)	0.126 (3)	0.378 (3)	9.3
C(48)	0.153 (5)	0.309 (3)	0.3269 (19)	8.7
C(49)	0.388 (7)	0.302 (4)	0.239 (3)	11.2
C(50)	0.478 (7)	0.132 (3)	0.199 (3)	11.2

[a] Given by B_{eq} only for Zr atom.

heavy-atom method and refined by full-matrix least squares as implemented in the X-ray System[50] utilizing observed relfections [$|F_o| > 3\sigma(F_o)$]. In the subsequent refinements, the function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factors amplitudes, respectively. The agreement indices are defined as $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|)^2]^{1/2}$ where $w^{-1} = \sigma^2(F_o) + g(F_o)^2$ ($g = 0.003$). After the anisotropic refinement of non-hydrogen atoms for **8**, **23a**, and **34**, all hydrogen atoms were located in the difference Fourier maps with the help of geometrical calculations and were refined isotropically. In the case of **24a**, after the anisotropic refinement for a Zr atom, the anisotropic refinement was extended stepwisely to the other non-hydrogen atoms. However, positive definite conditions were broken by some atoms in any trial due to the low quality of the diffraction data. Thus the anisotropic refinement was limited only to a Zr atom. Fractional atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms in **8**, **23a**, **24a**, and **34** are given in Tables IX, X, XI, and XII, respectively. The ORTEP drawings were obtained by using Johnson's program.[51]

All calculations were carried out on an ACOS-850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Preparation of $Cp^*_2Zr[C_4H_6C(=O)O]$ (8). Oxygen-free carbon dioxide was added to a stirred hexane solution (30 mL) of $ZrCp^*_2$(*s-trans*-butadiene) 2.0 g, 4.82 mmol) in a 100-mL two-necked flask by bubbling the gas with a flow rate of ca. 40 mL/min at 20–25 °C for 3 h. The mixture was stirred at 40 °C for 20 min and then evaporated to dryness. The product was extracted from the residue into tetrahydrofuran (10 mL). After concentration of the extract to 2 mL, hexane (4 mL) was added to induce the precipitation of the colorless crystals of the $ZrCp^*_2(C_4H_6)/CO_2$ (1:1) adduct at ambient temperature in 95% gas chromatographic yield. Further purification was made by recrystallization from THF/hexane: mp 172 °C; ^{13}C NMR (C_6D_6, J_{CH} in Hz) δ 11.35, 11.57 (C_5Me_5), 39.64 ($OCCH_2$, 127), 49.50 (CH_2, 148), 104.10 (CH, 154), 116.50, 116.94 (C_5Me_5), 128.48 (CH=, 142), 187.43 (CO); EIMS *m/z* (relative intensity) 462 (M^+; ^{94}Zr, 14.5), 460 (M^+; ^{92}Zr, 17.6), 459 (M^+; ^{91}Zr, 20.6), 458.1771 (M^+; ^{90}Zr, 40.6; calcd 458.1762), 360 ($ZrCp^*_2$; ^{90}Zr, 100); IR (neat) 1660 cm^{-1} (C=O). Anal. Calcd for $C_{25}H_{36}O_2Zr$: C, 65.31; H, 7.89. Found: C, 65.08; H, 7.91.

Preparation of $Cp^*_2Zr[OC(=O)C_5H_8C(=O)O]$ (12). Excess carbon dioxide was added to a stirred hexane solution (20 mL) of $ZrCp^*_2(C_5H_8)$ (2) (0.9 g, 2.0 mmol) with essentially the same procedure as described for the preparation of 8, after which the mixture was stirred at 40 °C for 1 h to complete the reaction. The color of the red-brown solution turned pale yellow during the reaction. Volatiles were removed by flash distillation, and the product was extracted into THF (10 mL). Concentration of the extract, followed by the addition of hexane (5 mL), gave the colorless microcrystals of the 1:2 adduct in 80% yield: mp 194 °C; ^{13}C NMR (C_6D_6) δ 11.7 (C_5Me_5), 12.1 (CH_3), 14.8 (CH_2CH=), 32.4 ($CH_2C(CH_3)$=), 118.7 ($CH=C(CH_3)$), 121.9 (C_5Me_5), 123.8 ($CH=C(CH_3)$), 173.8 and 173.7 (CO); IR (neat) 1660 cm^{-1} (C=O); EIMS *m/z* (relative intensity ratio) 520 (M^+; ^{94}Zr, 18.3), 518 (M^+; ^{92}Zr, 20.2), 517 (M^+; ^{91}Zr, 22.3), 516 (M^+; ^{90}Zr, 45.4), 476 ($M^+ - CO_2$; ^{94}Zr, 8.6), 474 ($M^+ - CO_2$, ^{92}Zr, 9.0), 473 ($M^+ - CO_2$; ^{91}Zr, 10.3), 472 ($M^+ - CO_2$; ^{90}Zr, 22.5). Anal. Calcd for $C_{27}H_{38}O_4Zr$: C, 62.63; H, 7.40. Found: C, 62.43; H, 7.67.

Preparation of 2:1 Adduct of $ZrCp_2$(diene) with CO_2. Dry carbon dioxide was added to a stirred hexane solution (20 mL) of $ZrCp_2(C_4H_6)$ (3) (0.5 g, 2.0 mmol) by using a flow rate of 30

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(51) Johnson, C. K. *ORTEP-II*, Report ORNL-5138; Oak Ridge National Laboratory, Oak Ridge, TN, 1974.

Table XII. Fractional Atomic Coordinates and B_{eq} for $Cp^*_2Zr[CH{=}C(CH_3)CH(CH_3)C({=}C(C_6H_5)_2)O]$ (34)

atom	x	y	z	B_{eq}, Å^2
Zr	0.20758 (4)	0.12059 (3)	0.33551 (3)	2.76
O(1)	0.2473 (3)	0.1052 (2)	0.2368 (2)	2.3
C(1)	0.0558 (5)	0.0432 (4)	0.2705 (4)	2.7
C(2)	0.0364 (5)	0.0087 (4)	0.1994 (4)	2.6
C(3)	0.1080 (5)	0.0191 (4)	0.1442 (4)	2.7
C(4)	0.0447 (6)	0.0795 (5)	0.0770 (4)	3.9
C(5)	−0.0694 (6)	−0.0458 (5)	0.1635 (4)	4.1
C(6)	0.2307 (5)	0.0482 (4)	0.1796 (3)	2.4
C(7)	0.3180 (5)	0.0267 (4)	0.1518 (4)	2.9
C(21)	0.1493 (5)	0.2626 (4)	0.2706 (3)	2.7
C(22)	0.2328 (5)	0.2768 (4)	0.3451 (4)	3.1
C(23)	0.1790 (6)	0.2569 (4)	0.4025 (4)	3.4
C(24)	0.0693 (6)	0.2265 (4)	0.3632 (4)	3.4
C(25)	0.0496 (5)	0.2311 (4)	0.2818 (4)	3.1
C(26)	0.1644 (7)	0.2867 (5)	0.1933 (4)	4.5
C(27)	0.3461 (7)	0.3180 (5)	0.3576 (5)	5.2
C(28)	0.2254 (8)	0.2833 (5)	0.4887 (4)	5.5
C(29)	−0.0224 (7)	0.2034 (6)	0.4010 (5)	5.8
C(30)	−0.0642 (6)	0.2162 (5)	0.2184 (5)	4.8
C(31)	0.3893 (5)	0.0416 (4)	0.4068 (4)	3.1
C(32)	0.3624 (6)	0.0897 (4)	0.4660 (4)	3.4
C(33)	0.2619 (6)	0.0560 (4)	0.4755 (4)	3.3
C(34)	2.2243 (6)	−0.0101 (4)	0.4232 (4)	3.5
C(35)	0.3032 (5)	−0.0195 (4)	0.3806 (4)	2.9
C(36)	0.4946 (6)	0.0535 (6)	0.3824 (5)	4.9
C(37)	0.4443 (8)	0.1505 (5)	0.5177 (5)	5.9
C(38)	0.2137 (9)	0.0747 (6)	0.5413 (5)	6.8
C(39)	0.1285 (8)	−0.0695 (6)	0.4205 (6)	6.3
C(40)	0.2992 (7)	−0.0881 (5)	0.3215 (4)	4.4
C(41)	0.3089 (6)	−0.0407 (4)	0.0937 (4)	3.6
C(42)	0.2811 (7)	−0.1230 (5)	0.1066 (5)	4.8
C(43)	0.2827 (8)	−0.1875 (6)	0.0535 (6)	6.3
C(44)	0.3110 (8)	−0.1686 (6)	−0.0121 (6)	6.4
C(45)	0.3413 (8)	−0.0902 (6)	−0.0268 (5)	5.9
C(46)	0.3415 (7)	−0.0246 (5)	0.0265 (4)	5.0
C(51)	0.4315 (5)	0.0684 (5)	0.1806 (4)	3.5
C(52)	0.5325 (6)	0.0210 (6)	0.2001 (4)	5.2
C(53)	0.6390 (8)	0.0600 (10)	0.2295 (6)	8.0
C(54)	0.6446 (9)	0.1452 (10)	0.2393 (6)	9.0
C(55)	0.5457 (9)	0.1957 (7)	0.2176 (6)	7.4
C(56)	0.4404 (6)	0.1544 (5)	0.1871 (4)	4.5

mL/min at 20 °C. Bubbling of the gas for 1 h resulted in the precipitation of the brown-yellow powder. After being filtered, the product was washed with hexane and recrystallized from hexane/THF at −20 °C to give the 2:1 adduct of **3** with CO_2 (**15a**) as pale yellow crystals in 45% yield: mp 116 °C dec; EIMS *m/z* (relative intensity) 600 (M$^+$; ^{94}Zr–^{94}Zr, 11.3), 597 (M$^+$; ^{91}Zr–^{94}Zr, 10.4), 596 (M$^+$; ^{92}Zr–^{92}Zr and ^{90}Zr–^{94}Zr, 11.3), 595 (M$^+$; ^{91}Zr–^{92}Zr, 11.6), 594 (M$^+$; ^{91}Zr–^{91}Zr and ^{90}Zr–^{92}Zr, 13.6), 593 (M$^+$; ^{90}Zr–^{91}Zr, 14.5), 592 (M$^+$; ^{90}Zr–^{90}Zr, 28.8); ^{1}H NMR (C_6D_6) δ 1.90 (d, 4 H, J = 8.2 Hz, $ZrCH_2$), 1.98 (d, 4 H, J = 8.2 Hz, $(O)_2CCH_2$), 5.29 (q, 2 H, J = 10.5 Hz, CH=CH), 1.86 (s, 10 H, C_5H_5), 5.98 (s, 10 H, C_5H_5), 6.51 (q, 2 H, CH=CH); ^{13}C NMR (C_6D_6) δ 40.6 (O_2CCH_2), 110.2 and 109.8 (Cp), 112.1 ($ZrCH_2$), 115.1 (CH=), 138.5 (CH=CH_2). Anal. Calcd for $C_{29}H_{32}O_2Zr_2$: C, 58.54; H, 5.42. Found: C, 57.95; H, 5.42.

The 2:1 adduct of $ZrCp_2(C_5H_8)$ (**4**) with carbon dioxide, **15b**/**16b**, was obtained in a similar manner as described for **15a** as colorless microcrystals in 78% yield: mp 117–123 °C dec; EIMS *m/z* (relative intensity) 628 (M$^+$; ^{94}Zr–^{94}Zr, 8.7), 625 (M$^+$; ^{94}Zr–^{91}Zr, 10.1), 624 (M$^+$; ^{94}Zr–^{90}Zr and ^{92}Zr–^{92}Zr, 13.8), 622 (M$^+$; ^{92}Zr–^{90}Zr, 13.0), 620 (M$^+$; ^{90}Zr–^{90}Zr, 23.4); ^{1}H NMR (C_6D_6) 1.85 (d, 4 H, $ZrCH_2$), 2.30, 2.28 (s, 6 H, CH_3), 5.1–5.2 (t, 2 H, CH=), 5.91, 5.98 (s, 20 H, C_5H_5). Anal. Calcd for $C_{31}H_{36}O_2Zr_2$: C, 59.76; H, 5.82. Found: C, 59.22; H, 5.75.

Reaction of (2-Methyl-2-butene-1,4-diyl)magnesium with CO_2. Carbon dioxide was bubbled into a stirred tetrahydrofuran solution (10 mL) of (2-methyl-2-butene-1,4-diyl)magnesium (5.0 mmol) at 0 °C by using a flow rate of 10 mL/min for 15 min. The color of the solution turned to pale orange from brown. Volatiles were removed by flash distillation in vacuo. After the addition of ether to the residue, the product was hydrolyzed with NaCl-saturated water and the ether layer was distilled in vacuo to give 2,2-dimethyl-3-butenoic acid in 70% yield. The addition of excess carbon dioxide to a tetrahydrofuran solution of (2-methyl-2-butene-1,4-diyl)magnesium (5 mmol) by using a flow rate of 30 mL/min at 25 °C, followed by evaporation of the mixture and hydrolysis in ether, gave a crude sample of 2-isopropenylsuccinic acid in ca. 70% yield. Dehydration occurs readily during the vacuum distillation of the dicarboxylic acid to give 2-isopropenylsuccinic anhydride in 65% yield.

Preparation of t-C_4H_9NCO Adduct of 1 (23a). To a THF solution (5 mL) of **1** (2.0 mmol) was added *t*-BuNCO (0.2 mL, 2.0 mmol) at −70 °C via syringe. The mixture was stirred at 30 °C for 5 h and evaporated to dryness. The product was extracted and purified by recrystallization from hexane–THF (6:1) at −20 °C: yield 87%; mp 130 °C; EIMS *m/z* (relative intensity) 517.2507 (M$^+$; ^{94}Zr, 31.1, calcd 517.2565), 515 (M$^+$; ^{92}Zr, 42.5), 514 (M$^+$; ^{91}Zr, 48.3), 513.2556 (M$^+$; ^{90}Zr, 84.7; calcd 513.2549), 498 (M$^+$ − CH_3; ^{90}Zr, 29.1), 360 (Cp^*_2Zr; ^{90}Zr, 48.3); ^{13}C NMR (C_6D_6, J_{CH} in Hz) δ 11.80, 11.61 (q, 125, Cp*), 49.86 (t, 128, CH_2C=N), 52.59 (t, 147, 1-CH_2), 32.73 (q, *t*-Bu), 43.09 (s, *t*-Bu), 106.47 (d, 152, 3-CH), 129.73 (d, 139, 2-CH), 116.76, 116.33 (s, Cp*), 178.36 (s, C=N). Anal. Calcd for $C_{29}H_{45}NOZr$: C, 67.65; H, 8.81; N, 2.72. Found: C, 67.28; H, 8.96; N, 2.52. Acid cleavage of **23a** gave *N*-*tert*-butyl-4-pentenamide: ^{1}H NMR ($CDCl_3$) δ 1.34 (s, 9 H, *t*-Bu), 2.22 (m, 2 H, CH_2), 2.34 (t, 2 H, CH_2CO), 5.01, 5.05 (dd, 2 H, J = 9.8 and 17.8 Hz, CH_2=), 5.42 (b s, 1 H, NH), 5.84 (m, 1 H, J = 6.8 Hz, CH=); EIMS *m/z* 155 (M$^+$).

Preparation of t-C_4H_9NCO Adduct of 3 (23b). The product was obtained in a similar manner as described for **23a** as colorless crystals in 72% yield: mp 182 °C; EIMS *m/z* (relative intensity) 377 (M$^+$; ^{94}Zr, 22.5), 375 (M$^+$; ^{92}Zr, 30.3), 374 (M$^+$; ^{91}Zr, 32.4), 373 (M$^+$; ^{90}Zr, 68.9), 220 (Cp_2Zr; ^{90}Zr, 100). Anal. Calcd for $C_{19}H_{25}NOZr$: C, 60.91; H, 6.73; N, 3.74. Found: C, 60.19; H, 7.24; N, 3.53.

Preparation of C_6H_5NCO Adduct of 1 (23c). A hexane solution (6 mL) of **1** (2.0 mmol) and C_6H_5NCO (2.0 mmol) was stirred at 40 °C for 2 h, yielding the adduct **23c** as pale yellow crystals in 60% yield by recrystallization of the product from hexane: mp 167 °C; EIMS *m/z* (relative intensity) 537 (M$^+$; ^{94}Zr, 19.8), 535 (M$^+$; ^{92}Zr, 31.1), 534 (M$^+$; ^{91}Zr, 32.9), 533 (M$^+$; ^{90}Zr, 78.2), 518 (M$^+$ − CH_3; ^{90}Zr, 16.8), 360 (Cp^*_2Zr; ^{90}Zr, 100). Anal. Calcd for $C_{31}H_{41}NOZr$: C, 69.61; H, 7.73; N, 2.62. Found: C, 69.33; H, 7.81; N, 2.45. Acid cleavage of **40c** gave *N*-phenyl-4-pentenamide: ^{1}H NMR ($CDCl_3$) δ 2.62 (m, 2 H, CH_2), 3.17 (t, 2 H, J = 4.5 Hz, CH_2O), 5.29, 5.32 (dd, 2 H, CH_2=), 6.04 (m, 1 H, J = 7.4 Hz, CH=), 6.70 (b s, 1 H, NH), 7.12–7.56 (m, 5 H, C_6H_5); EIMS *m/z* 175 (M$^+$).

Preparation of C_6H_5NCO Adduct of 3 (23d). The product was obtained as colorless crystals in 75% yield from the reaction of **3** (2.0 mmol) with C_6H_5NCO (2.0 mmol) in THF, followed by recrystallization of the product from hexane–THF: mp 190 °C; EIMS *m/z* (relative intensity) 397 (M$^+$; ^{94}Zr, 8.8), 395 (M$^+$; ^{92}Zr, 11.2), 394 (M$^+$, ^{91}Zr, 12.3), 393 (M$^+$; ^{90}Zr, 29.8), 220 (Cp_2Zr; ^{90}Zr, 100). Anal. Calcd for $C_{21}H_{21}NOZr$: C, 63.92; H, 5.36; N, 3.55. Found: C, 63.41; H, 5.30; N, 3.52.

Preparation of 1:2 Adduct of 1 with C_6H_5NCO (24a). The butadiene complex **1** (2.0 mmol) was allowed to react with C_6H_5NCO (0.4 mL, 4.0 mmol) in THF at 30 °C for 5 h. Crystallization of the product from hexane at 0 °C gave **24a** as colorless crystals in 72% yield: mp 202 °C; EIMS *m/z* (relative intensity) 656 (M$^+$; ^{94}Zr, 19.0), 654 (M$^+$; ^{92}Zr, 26.5), 653 (M$^+$; ^{91}Zr, 34.9), 652 (M$^+$; ^{90}Zr, 50.8), 517 (M$^+$ − C_5Me_5; ^{90}Zr, 85.9), 376 (Cp^*_2ZrO; ^{90}Zr, 100); ^{13}C NMR (C_6D_6, J_{CH} in Hz) δ 31.92 (t, 129, CH_2), 130.2 (d, 157, CH=), 164.9 (s, C=N), 11.50, 122.77 (Cp*). Anal. Calcd for $C_{38}H_{46}N_2O_2Zr$: C, 69.79; H, 7.09; N, 4.28. Found: C, 69.18; H, 7.36; N, 4.20. Acid cleavage of **41a** gave (*E*)-$C_6H_5NHCOCH_2CH{=}CHCH_2CONHC_6H_5$ in 90% yield: ^{1}H NMR ($CDCl_3$) δ 3.23 (m, 4 H, CH_2), 5.90 (m, 2 H, J = 15.3 Hz, CH=CH), 6.67 (b s, 2 H, NH), 7.21–7.55 (m, 10 H, C_6H_5).

Preparation of 1:2 Adduct of 3 with C_6H_5NCO (24b). Prepared in a similar manner as described for **24a**; mp 210 °C. ^{1}H NMR spectral data are given in Table VII.

Preparation of t-C_4H_9NCO Adduct of 2 (25a). To a hexane solution (6 mL) of **2** (2.0 mmol) was added t-C_4H_9NCO (0.2 mL, 2.0 mmol) at 0 °C. The mixture was stirred at 30 °C for 3 h and then concentrated. Cooling of the solution to −20 °C gave **25a** as colorless crystals in 65% yield: mp 162 °C; EIMS *m/z* (relative intensity) 531 (M^+; ^{94}Zr, 23.2), 529 (M^+; ^{92}Zr, 25.4), 528 (M^+; ^{91}Zr, 31.2), 527 (M^+; ^{90}Zr, 72.6), 360 (Cp^*_2Zr, 100). Anal. Calcd for $C_{30}H_{47}NOZr$: C, 68.12; H, 8.96; N, 2.65. Found: C, 67.10; H, 8.65; N, 2.66.

Preparation of *t*-C_4H_9NCO Adduct of 4 (25b). The adduct was obtained as colorless crystals in 70% yield by the 1:1 reaction of *t*-C_4H_9NCO with **4** at 30 °C for 5 h followed by recrystallization from hexane at -20 °C: mp 159 °C; EIMS *m/z* (relative intensity) 391 (M^+; ^{94}Zr, 27.7), 389 (M^+; ^{92}Zr, 28.8), 388 (M^+; ^{91}Zr, 38.9), 387 (M^+; ^{90}Zr, 78.8), 220 (Cp_2Zr; ^{90}Zr, 100). Anal. Calcd for $C_{20}H_{27}NOZr$: C, 61.81; H, 7.00; N, 3.60. Found: C, 60.41; H, 6.83; N, 3.63.

Preparation of 1:2 Adduct of 2 with C_6H_5NCO (28a). Complex **2** (2.0 mmol) was allowed to react with phenyl isocyanate (4.0 mmol) in hexane at 60 °C for 3 h. The product **45a** was isolated as colorless crystals in 65% yield: mp 218 °C; EIMS *m/z* (relative intensity) 670 (M^+; ^{94}Zr, 7.6), 668 (M^+; ^{92}Zr, 11.5), 667 (M^+; ^{91}Zr, 12.7), 666 (M^+; ^{90}Zr, 18.1), 531 ($M^+ - Cp^*$; ^{90}Zr, 36.0), 376 (Cp^*_2ZrO; ^{90}Zr, 100). Anal. Calcd for $C_{39}H_{48}N_2O_2Zr$: C, 70.12; H, 7.24; N, 4.19. Found: C, 71.20; H, 7.30; N, 4.23.

Preparation of 1:2 Adduct of 6 with C_6H_5NCO (28b). Prepared in a similar manner as described for **28a**; mp 221 °C; ^1H NMR (C_6D_6) δ 1.72 (s, 3 H, CH_3), 2.80 (d, 2 H, CH_2), 2.94 (b s, 2 H, CH_2), 5.10 (t, 1 H, CH), 5.98 (s, 10 H, Cp), 7.15–7.55 (m, 10 H, C_6H_5).

Preparation of $CH_3(C_6H_5)CCO$ Adduct of 1 (29a). To a hexane solution (6 mL) of **1** (2.0 mmol) was added methylphenylketen[52] (0.2 mL, 2.0 mmol) at -70 °C. The mixture was allowed to warm to room temperature and kept there for 3 h with magnetic stirring. Concentration of the solution followed by cooling to -20 °C gave **30a** as pale yellow crystals in ca. 50% yield: mp 139 °C; EIMS *m/z* (relative intensity) 550 (M^+, ^{94}Zr, 9.8), 548 (M^+; ^{92}Zr, 12.3), 547 (M^+; ^{91}Zr, 11.1), 546 (M^+; ^{90}Zr, 20.3), 411 ($M^+ - Cp^*$; ^{90}Zr, 62.7), 360 (Cp^*_2Zr; ^{90}Zr, 31.4), 241 (Cp^*ZrO; ^{90}Zr, 100). Anal. Calcd for $C_{33}H_{44}OZr$: C, 72.34; H, 8.09. Found: C, 70.91; H, 7.98.

Preparation of $CH_3(C_6H_5)CCO$ Adduct of 2 (30b). Prepared in a similar manner as described for **30a** and isolated as colorless crystals in 80% yield: mp 118 °C; EIMS *m/z* (relative intensity) 564 (M^+; ^{94}Zr, 1.4), 562 (M^+; ^{92}Zr, 5.1), 561 (M^+; ^{91}Zr, 5.0), 560 (M^+; ^{90}Zr, 11.7), 425 ($M^+ - Cp^*$; ^{90}Zr, 83.4), 360 (Cp^*_2Zr; ^{90}Zr, 30.9), 241 (Cp^*ZrO; ^{90}Zr, 100). Anal. Calcd for $C_{34}H_{46}OZr$: C, 72.67; H, 8.25. Found: C, 71.93; H, 7.94.

Preparations of 1:2 Adduct of $CH_3(C_6H_5)CCO$ (31a,b). The adduct was prepared from the reaction of **3** or **4** (2.0 mmol) with methylphenylketene (4.0 mmol) in hexane: $CH_3(C_6H_5)CCO/3$, mp 182 °C; $CH_3(C_6H_5)CCO/4$, mp 195 °C. ^1H NMR data are given in Table VII.

Preparation of $Cp^*_2Zr[OC(=C(C_6H_5)_2)CH(CH_3)C(CH_3)=CH]$ (34). Diphenylketene (0.3 mL, 2.0 mmol), synthesized according to the reported method,[53] was added to a hexane solution (6 mL) of the isoprene complex **2** at -70 °C. The mixture was allowed to warm to room temperature and stirred there for 3 h with magnetic stirring. The solution was then concentrated and cooled to -20 °C to induce the precipitation of **34** as pale yellow crystals in ca. 80% yield: mp 113 °C; EIMS *m/z* (relative intensity) 626.2744 (M^+; ^{94}Zr, 10.4; calcd 626.2768), 624 (M^+; ^{92}Zr, 15.4), 623 (M^+; ^{91}Zr, 19.8), 622.2717 (M^+; ^{90}Zr, 29.8; calcd 622.2753), 487 ($M^+ - Cp^*$; ^{90}Zr, 30.5), 241 (Cp^*ZrO; ^{90}Zr, 100); ^1H NMR (C_6D_6) δ 1.39 (d, 3 H, *J* = 7.0 Hz, CH_3), 1.99 (s, 3 H, $CH_3C=$), 3.77 (q, 1 H, CH), 6.00 (s, 1 H, ZrCH=), 1.90, 1.69 (s, 10 H, Cp); ^{13}C NMR (C_6D_6, J_{CH} in Hz) δ 181.06 (d, 150, C-1), 135.64 (s, C-2), 21.68 (q, 2-CH_3), 46.63 (d, 135, C-3), 29.35 (q, C-4), 128.22 (s, C-5), 128.38 (s, C-6), 11.04, 11.34 (q, Cp*), 118.98, 119.44 (s, Cp*). Anal. Calcd for $C_{39}H_{48}OZr$: C, 75.06; H, 7.75. Found: C, 74.41; H, 7.66.

Preparation of $Cp^*_2Zr[OC(=C(C_6H_5)_2)CH(CH_2D)C(CH_3)=CD]$ (34-d_2). The precursor $CD_2=C(CH_3)CH=CH_2$ was prepared by the pyrolysis of $CH_2=CHCH(CH_3)CD_2OCOCH_3$, which is obtained by the reaction of $CH_2=CHCH(CH_3)COOC_2H_5$[54] with $LiAlD_4$. To a THF (10 mL) solution of $Cp^*_2ZrCl_2$ (0.6 g, 1.2 mmol) was added a THF suspension of $[MgCH_2CH=C(CH_3)CD_2]_n$ (1.2 mmol) at -78 °C. $Cp^*_2Zr(C_5H_6D_2)$ was obtained as orange crystals by the recrystallization from hexane. **34**-d_2 was prepared in the same manner as described for **34**: yield ca. 80%; mp 115 °C.

Preparation of 1:2 Adduct of 3 with $(C_6H_5)_2CCO$ (39a). The butadiene complex **3** (2.0 mmol) was allowed to react with $(C_6H_5)_2CCO$ (4.0 mmol) in THF at 30 °C for 4 h. Crystallization of the product from THF/hexane (5:1) gave **39a** as colorless crystals in 55% yield: mp 205 °C; EIMS *m/z* (relative intensity) 666 (M^+; ^{94}Zr, 10.5), 664 (M^+; ^{92}Zr, 13.1), 663 (M^+; ^{91}Zr, 15.2), 662 (M^+; ^{90}Zr, 28.6), 597 ($M^+ - Cp$; ^{90}Zr, 7.9), 220 (Cp_2Zr; ^{90}Zr, 100). Anal. Calcd for $C_{42}H_{36}O_2Zr$: C, 75.98; H, 5.47. Found: C, 74.84; H, 5.32.

Preparation of 1:2 Adduct of 6 with $(C_6H_5)_2CCO$ (39b). The product was obtained in a similar manner as described for **39a** as colorless crystals in 60% yield: mp 215 °C; EIMS *m/z* (relative intensity) 680 (M^+; ^{94}Zr, 15.1), 678 (M^+; ^{92}Zr, 20.2), 677 (M^+; ^{91}Zr, 20.1), 676 (M^+; ^{90}Zr, 38.2), 611 ($M^+ - Cp$; ^{90}Zr, 5.5), 220 (Cp_2Zr; ^{90}Zr, 100). Anal. Calcd for $C_{43}H_{38}O_2Zr$: C, 76.18; H, 5.65. Found: C, 75.88; H, 5.23.

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Supplementary Material Available: Tables of final atomic coordinates for non-hydrogen and hydrogen atoms with thermal parameters and bond distances and angles including hydrogen atoms (20 pages); listings of observed and calculated structure factors (162 pages). Ordering information is given on any current masthead page.

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