

# Unique Chemical Behavior and Bonding of Early-Transition-Metal-Diene Complexes

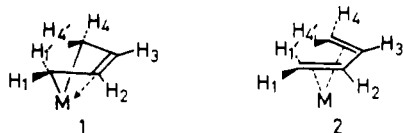
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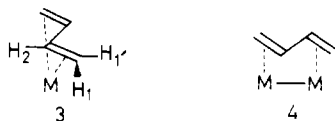
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(Diene)metal complexes have given us a distinctive chemistry for a vast class of organometallic compounds. Recently this chemistry entered on a new phase with the advent of highly reactive group 4 and 5<sup>33</sup> early-transition-metal congeners. These compounds exhibit a unique structural pattern together with unusually high selectivity, as observed in reactions with organic substrates with C-C, C-O, and C-N unsaturation.

The characteristics of early transition metals are exemplified in the structure of their diene complexes, and unique *s-cis* and novel *s-trans* coordination of dienes have recently been found. The bent *s-cis*-metal-lacyclo-3-pentene structure (1), which emphasizes the  $\sigma$ -bonding at the diene termini and  $\pi$ -bonding at the inner carbon atoms, has been established based on the X-ray structure determinations of  $Zr(\eta-C_5R_5)_2(\text{diene})$ ,<sup>1</sup>  $Hf(\eta-C_5R_5)_2(\text{diene})$ ,<sup>2</sup>  $Ta(\eta-C_5R_5)Cl_2(\text{diene})$ ,<sup>3</sup> and  $Ta(\eta-C_5R_5)(\text{diene})_2$ .<sup>3</sup> The vast majority of transition-metal-diene complexes reported so far can be expressed essentially in the form of the metal species coordinated by *s-cis*- $\eta^4$ -diene (2) as found for  $Fe(CO)_3(C_4H_6)$ ,<sup>4</sup>  $RhCl(C_4H_6)_2$ ,<sup>5</sup> etc.



The *s-trans*- $\eta^4$ -diene coordination to mononuclear metal species (3) first appeared for the diene complexes of group 4 metals ( $Zr^6$  and  $Hf^7$ ), though the *s-trans*-diene coordination had been reported for binuclear metal complexes of type 4 and for a trinuclear osmium complex. This finding provided us further information



on the stereochemistry of the oligomerization and polymerization of dienes catalyzed by Ziegler-Natta catalyst systems. For example, the significance of the *s-trans*- $\eta^4$ -diene coordination to metal has been stressed to account for the stereoselective 1,4-trans polymerization of butadiene with  $TiCl_4/AlEt_3$ .<sup>8a</sup> Until recently, only  $\eta^2$ -diene coordination had been proposed to interpret the reaction mechanism.<sup>8b,c</sup>

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**Table I.**  
Bond Distances (Å) and Torsional Angles ( $\phi$  deg) for (*s-cis*-Diene)metal Complexes

	M-C <sub>1</sub>	M-C <sub>2</sub>	C <sub>1</sub> -C <sub>2</sub>	C <sub>2</sub> -C <sub>3</sub>	$\phi$
ZrCp <sub>2</sub> (DM) <sup>a</sup>	2.300	2.597	1.451	1.398	126.9
Hr(dmpe)(C <sub>4</sub> H <sub>6</sub> )	2.353	2.407	1.428	1.376	
TaCp(DM) <sub>2</sub>	2.262	2.523	1.469	1.352	102.5
	2.292	2.473	1.475	1.343	100.4
TaCpCl <sub>2</sub> (C <sub>4</sub> H <sub>6</sub> )	2.258	2.424	1.458	1.375	94.9
TaCp*Cl <sub>2</sub> (C <sub>4</sub> H <sub>6</sub> ) <sup>b</sup>	2.217		1.552	1.553	116.3
RhCl(C <sub>4</sub> H <sub>6</sub> ) <sub>2</sub>	2.21	2.15	1.38	1.45	85.1
Fe(CO) <sub>3</sub> (C <sub>4</sub> H <sub>6</sub> )	2.14	2.06	1.45	1.45	71.2

<sup>a</sup>DM = 2,3-dimethylbutadiene. <sup>b</sup>Tantalacyclopentane in ref 32.

## Synthetic Approaches

Most diene complexes reported so far have been synthesized by direct reaction of 1,3- or 1,4-dienes with thermally rather stable low-valent metal species. However, the synthesis of the corresponding diene complexes of group 4-6 metals generally required novel synthetic routes as summarized below, since the generation of low-valent metal species is much more difficult: (1) reaction of cyclopentadienylmetal halides, metal halides, or metal alkoxides with bifunctional endiylmagnesium,  $(-MgCH_2CR=CRCH_2-)_n$ ,<sup>9</sup> (2) photolysis of diarylmetallocene in the presence of conjugated dienes,<sup>6b</sup> (3) oxidative addition of conjugated dienes on the low-valent metal species generated by reduction of metal halides with Na amalgam or lithium,<sup>10</sup> (4)  $\sigma, \pi$ -rearrangement of hydrido( $\sigma$ -pentadienyl)metal species generated by treating  $L_nMHCl$  with pentadienyl anions;<sup>11</sup> (5) substitution of the diene ligand with more

(1) (a) Erker, G.; Engel, K.; Krüger, C.; Chiang, A.-P. *Chem. Ber.* **1982**, *115*, 3311. (b) Lubke, B.; Edelmann, F.; Behrens, U.; *Ibid.* **1983**, *116*, 11.

(2) Krüger, C.; Müller, G.; Erker, G.; Dorf, U.; Engel, K. *Organometallics* **1985**, *4*, 215.

(3) (a) For a preliminary report: Yasuda, H.; Mashima, K.; Okamoto, T.; Nakamura, A. Proceedings of 11th International Conference on Organometallic Chemistry, Atlanta, GA, 1983; Abstract, p 79. (b) Yasuda, H.; Tatsumi, K.; Okamoto, T.; Mashima, K.; Lee, K.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.*, in press.

(4) Mills, O. S.; Robinson, G. *Proc. Chem. Soc.* **1960**, 421.

(5) Immiriz, A.; Allegra, G. *Acta Crystallogr., Sect. B* **1969**, *B25*, 120.

(6) (a) Kai, Y.; Kanehisa, N.; Miki, K.; Kasai, N.; Mashima, K.; Nagasuna, K.; Yasuda, H.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1982**, 191. (b) Erker, G.; Wicher, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W.; Krüger, C. *J. Am. Chem. Soc.* **1980**, *102*, 6346. (c) Erker, G.; Wicher, J.; Engel, K.; Krüger, C. *Chem. Ber.* **1982**, *115*, 3300.

(7) Benn, R.; Schroth, G. *J. Organomet. Chem.* **1982**, *228*, 71.

(8) (a) Nakamura, A.; Yasuda, H.; Tatsumi, K. 33th Polymer Symposium, Japan, Preprint, S1D08. (b) Furukawa, J. *Acc. Chem. Res.* **1980**, *13*, 1. (c) Porri, L.; Gallazzi, M. C.; Destri, S.; Bolonesi, A. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 485.

(9) (a) Yasuda, H.; Kajihara, Y.; Mashima, K.; Nagasuna, K.; Lee, K.; Nakamura, A. *Organometallics* **1982**, *1*, 388. (b) Yasuda, H.; Kajihara, Y.; Mashima, K.; Lee, K.; Nakamura, A. *Chem. Lett.* **1981**, 519.

(10) (a) Wreford, S. S.; Whitney, J. F. *Inorg. Chem.* **1981**, *20*, 3918. (b) Datta, S.; Fischer, M. B.; Wreford, S. S. *J. Organomet. Chem.* **1980**, *188*, 353. (c) Beatty, P. P.; Datta, S.; Wreford, S. S. *Inorg. Chem.* **1979**, *18*, 3139.

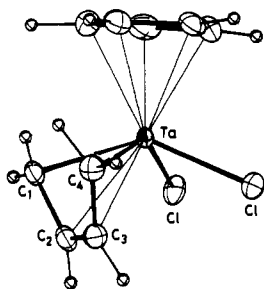
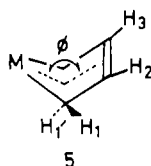


Figure 1. Molecular structure of TaCpCl<sub>2</sub>(butadiene).

$\pi$ -acidic dienes;<sup>9</sup> (6) coupling of dialkenyl groups in the coordination sphere of the metal species;<sup>12</sup> (7) cocondensation of metal vapor with conjugated dienes at low temperature.<sup>13</sup>

### Significant Features in the Structure and Bonding of *s-cis*-Diene Complexes

ZrCp<sub>2</sub>(2,3-dimethylbutadiene), ZrCp<sub>2</sub>(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>), and ZrCp<sub>2</sub>(2,3-diphenylbutadiene) are among the well-characterized metal-diene complexes of group 4 elements which possess the *s-cis* bent metallacyclo-3-pentene structure (1).<sup>1,2</sup> The bent angle ( $\phi$ ) between the planes defined by C<sub>1</sub>ZrC<sub>4</sub> and C<sub>1</sub>C<sub>2</sub>C<sub>3</sub>C<sub>4</sub> atoms is 120–127°, and the bond distances of Zr–C<sub>1</sub> (Zr–C<sub>4</sub>) (2.29–2.30 Å) are shorter than those of Zr–C<sub>2</sub> (Zr–C<sub>3</sub>) (2.60–2.86 Å). The inner bond C<sub>2</sub>–C<sub>3</sub> (1.39–1.42 Å) is significantly shorter than the C<sub>1</sub>–C<sub>2</sub> or the C<sub>3</sub>–C<sub>4</sub> bonds (1.45–1.48 Å) but is still longer than the normal C–C double bond (Table I).



Though zirconium complexes often show fluxional behavior, TaCpCl<sub>2</sub>(butadiene), a group 5 metal complex, has a more rigid bent metallacyclo-3-pentene structure even at high temperatures (Figure 1). The bent angle (95°) is smaller than that for zirconium derivatives. The C<sub>2</sub>–C<sub>3</sub> bond (1.458 Å) is shorter than the C<sub>1</sub>–C<sub>2</sub> or C<sub>3</sub>–C<sub>4</sub> bonds by 0.08 Å, and the Ta–C<sub>1</sub> (Ta–C<sub>4</sub>) bond (2.258 Å) is shorter than Ta–C<sub>2</sub> (Ta–C<sub>3</sub>) bond by 0.13 Å. The observed bond distances and bent angles for Zr(diene) and Ta(diene) complexes significantly differ from those in diene complexes of later transition metals. For example, Fe(CO)<sub>3</sub>(C<sub>4</sub>H<sub>6</sub>) assumes the small bent angle (71°), and the metal is equidistant from the four carbons of the diene. The X-ray structure of Mg(PhCHCHCHPh)(THF)<sub>3</sub><sup>14</sup> resembles that of ZrCp<sub>2</sub>(*s-cis*-diene), but the nature of the M-diene interactions should be different between them because of the stronger ionic character of the Mg ion.

(11) (a) Nakamura, A.; Yasuda, H.; Tatsumi, K.; Noda, I.; Mashima, K.; Akita, M.; Nagasuna, K. "Organometallic Compounds, Synthesis, Structure and Theory"; Shapiro, B. L., Ed.; Texas A&M University: College Station, TX, 1983; Vol. 1. (b) Yasuda, H.; Nagasuna, K.; Akita, M.; Lee, K.; Nakamura, A. *Organometallics* 1984, 3, 1470.

(12) (a) Zisch, P.; Erker, G. *Organometallics* 1984, 3, 946. (b) R. Reckhans and Thiele, K.-H. *J. Organomet. Chem.* 1984, 263, C7.

(13) Skell, P. S.; McGlinchey, M. J. *Angew. Chem., Int. Ed. Engl.* 1975, 14, 195.

(14) Kai, Y.; Kanehisa, N.; Miki, K.; Kasai, N.; Mashima, K.; Yasuda, H.; Nakamura, A. *Chem. Lett.* 1982, 1277.

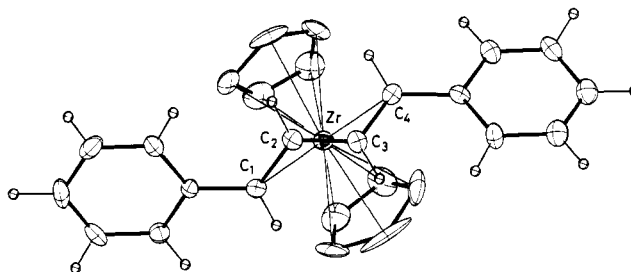


Figure 2. Molecular structure of ZrCp<sub>2</sub>(*s-trans*-1,4-diphenylbutadiene).

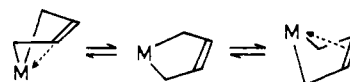
Table II.  
Selected Bond Distances (Å) for (*s-trans*-Diene)metal Complexes

	M–C <sub>1</sub>	M–C <sub>2</sub>	C <sub>1</sub> –C <sub>2</sub>	C <sub>2</sub> –C <sub>3</sub>
ZrCp <sub>2</sub> (BD) <sup>a</sup>	2.48	2.33		
ZrCp <sub>2</sub> (DP) <sup>b</sup>	2.51	2.40	1.44	1.47
Mn <sub>2</sub> (CO) <sub>8</sub> (BD)	2.23	2.30	1.39	1.39
Os <sub>3</sub> (CO) <sub>10</sub> (BD)	2.25	2.26	1.32	1.35
Mn <sub>2</sub> Cp <sub>2</sub> (CO) <sub>4</sub> (BD)	2.20	2.29	1.43	1.50

<sup>a</sup>BD = butadiene. <sup>b</sup>DP = 1,4-diphenylbutadiene.

<sup>13</sup>C and <sup>1</sup>H NMR parameters also revealed strong  $\sigma$ -bonding character of the early-transition-metal-diene complexes. When the spectra of Si(CH<sub>3</sub>)<sub>2</sub>(C<sub>4</sub>H<sub>6</sub>),<sup>15</sup> TaCpCl<sub>2</sub>(C<sub>4</sub>H<sub>6</sub>),<sup>3</sup> ZrCp<sub>2</sub>(C<sub>4</sub>H<sub>6</sub>),<sup>9a</sup> HfCp<sub>2</sub>(C<sub>4</sub>H<sub>6</sub>),<sup>9b</sup> and Fe(CO)<sub>3</sub>(C<sub>4</sub>H<sub>6</sub>)<sup>16</sup> are compared, the magnitude of the <sup>13</sup>C–<sup>1</sup>H coupling constant for the terminal carbons increases from 125 to 168 Hz in the order Si < Hf < Zr < Ta < Fe  $\approx$  Rh, indicating that the  $\sigma$ -bonding character decreases in this order. The <sup>1</sup>H NMR parameters for these complexes also support the above prediction; i.e., the absolute values of the geminal coupling constant ( $J_{1,1}$ ) for terminal CH<sub>2</sub> of Cp<sub>2</sub>Zr(C<sub>4</sub>H<sub>6</sub>) (–10.0 Hz) and CpTaCl<sub>2</sub>(C<sub>4</sub>H<sub>6</sub>) (–6.5 Hz) are considerably larger than that for Fe(CO)<sub>3</sub>(C<sub>4</sub>H<sub>6</sub>) (–2.4 Hz). The magnitude of the vicinal coupling constant ( $J_{1,2}$ ) also varies by changing the metal. The values of vicinal trans <sup>3</sup>J<sub>1,2</sub> are generally larger than those of cis <sup>3</sup>J<sub>1,2</sub> for diene complexes of the type 2 (M = Fe, Rh, Ru), while the relative order is reversed as <sup>3</sup>J<sub>1,2</sub> < <sup>3</sup>J<sub>1,2</sub> in the case of TaCpCl<sub>2</sub>(butadiene),<sup>3</sup> Ta(C<sub>5</sub>Me<sub>5</sub>)(C<sub>4</sub>H<sub>8</sub>)(C<sub>4</sub>H<sub>6</sub>),<sup>17</sup> and Hf(COT)(C<sub>4</sub>H<sub>6</sub>).<sup>18</sup> This change is ascribable to the bending of the five-membered metallacycle; i.e., the magnitude of <sup>3</sup>J<sub>1,2</sub> decreases as the terminal proton (H<sub>1</sub>) bends out of the C<sub>1</sub>–C<sub>2</sub>–C<sub>3</sub>–C<sub>4</sub> plane.

ZrCp<sub>2</sub>(diene) and HfCp<sub>2</sub>(diene) often show fluxional behavior, and the following topomerization proceeding through a planar metallacyclopentene transition state has been proposed.<sup>1,9</sup> The activation barrier for the



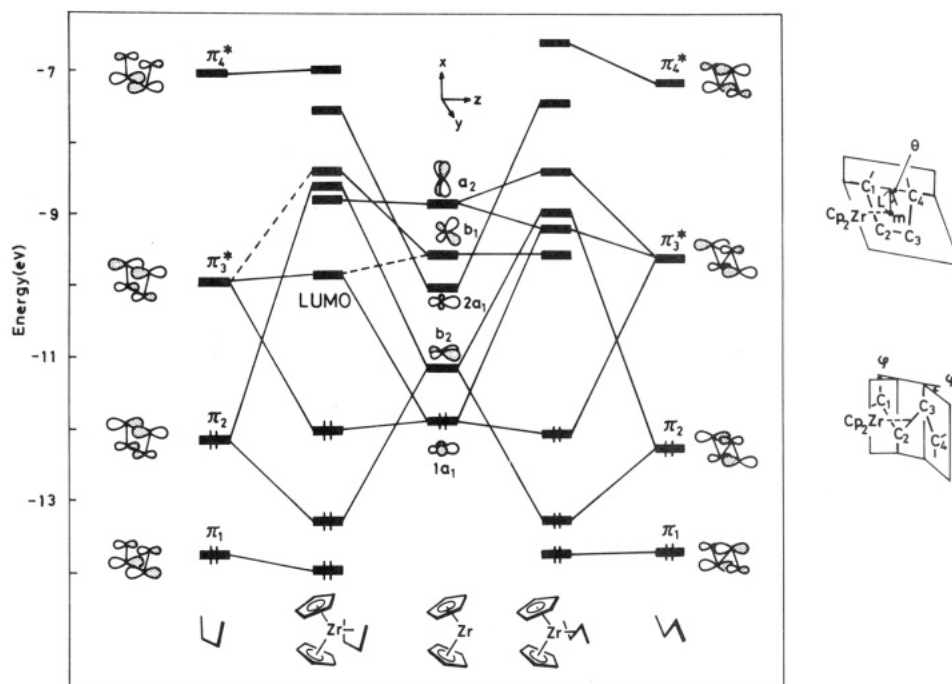
fluxionalization varies between 6.5 and 12.4 kcal/mol,<sup>1,2</sup> depending upon the bulkiness of the diene ligands. The planar metallacycle will be an active species in reactions with electrophiles as described later.

(15) (a) Panasenko, A. A.; Khalilov, L. M.; Tsyrina, E. M.; Yurev, V. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1981, 424. (b) Filleux-Blanchard, M. L.; Nguyen, D. A.; Manuel, G. *J. Organomet. Chem.* 1977, 137, 11.

(16) Bachmann, K.; von Philipsborn, W. *Organomet. Chem.* 1976, 8, 648.

(17) Mayer, J. M.; Curtis, C. J.; Bercaw, J. E. *J. Am. Chem. Soc.* 1983, 105, 2651.

(18) Wilke, G., unpublished work, cited in ref 7.



**Figure 3.** Orbital interaction diagrams for  $\text{ZrCp}_2$  and butadiene in *s-cis* structure ( $L = 0.3 \text{ \AA}$ ;  $\theta = 30^\circ$ ) and in *s-trans* structure ( $\phi = 15^\circ$ ). Geometrical variables used for the optimization of each structure are shown to the right of the diagrams.

### Characteristics in the Structures of (*s-trans*- $\eta^4$ -Diene)metal Complexes

The unique *s-trans* coordination of dienes to mononuclear metal species has been confirmed by the X-ray structural analysis of  $\text{ZrCp}_2(1,4\text{-diphenylbutadiene})^{6a}$  (see Figure 2) and  $\text{ZrCp}_2(\text{butadiene})^{6b,c}$ . The significant features of the  $\text{Zr}(s\text{-trans}\text{-}1,4\text{-diphenylbutadiene})$  complex lie in the following: (1) The four carbon atoms of the diene deviate from planarity to assume the torsional angle of ca.  $126^\circ$  between  $\text{C}_1\text{-C}_2$  and  $\text{C}_3\text{-C}_4$  bonds. (2) The ligand shows enhanced bond alternation ( $\text{C}_1\text{-C}_2 < \text{C}_2\text{-C}_3$ ) (see Table II). The respective bond distances compare closely to those in  $\text{Mn}_2\text{Cp}_2(\text{CO})_4(\text{C}_4\text{H}_6)^{19a}$  but differ from those for  $\text{Mn}_2(\text{CO})_8(\text{C}_4\text{H}_6)^{19b}$ ,  $\text{Re}_2(\text{CO})_8(\text{C}_4\text{H}_6)^{19c}$  and  $\text{Os}_3(\text{CO})_{10}(\text{C}_4\text{H}_6)^{19d,e}$  which show diminished bond alternation. (3) The  $\text{M-C}_1$  ( $\text{M-C}_4$ ) bond is significantly longer than the  $\text{M-C}_2$  ( $\text{M-C}_3$ ) bond, while the above noted binuclear and trinuclear complexes show the relation that the  $\text{M-C}_1$  ( $\text{M-C}_4$ ) bond distance is less than or equal to the  $\text{M-C}_2$  ( $\text{M-C}_3$ ) bond distance.

The mode of coordination, *s-trans* or *s-cis*, of conjugated dienes is controlled not only kinetically but also thermodynamically. In general, butadiene and its higher homologues bearing alkyl or aryl substituents on the  $\text{C}_1$  and/or  $\text{C}_4$  carbons kinetically favor the coordination in the *s-trans* form,<sup>9,20</sup> while substitution at the  $\text{C}_2$  and/or  $\text{C}_3$  atoms always brings about the predominance of *s-cis* coordination. Thus kinetic control is essential to determine the *s-cis/s-trans* ratio (Table III). However, the *s-trans* isomer in some cases converts to the more thermally stable *s-cis* isomer on heating in solution. The activation barrier ( $\Delta G^\ddagger$ ) for the interconversion of  $\text{ZrCp}_2(\text{butadiene})$  is calculated to be 23 kcal/mol and that for  $\text{Zr}(\text{C}_5\text{Me}_5)_2(\text{butadiene})$  is esti-

**Table III.**  
***s-Cis/s-Trans* Ratio (%) for  $\text{ZrCp}_2(\text{R}^1\text{CH}=\text{CR}^2\text{CR}^3=\text{CHR}^4)$  in  $\text{C}_6\text{D}_6$**

$\text{R}^1$	$\text{R}^2$	$\text{R}^3$	$\text{R}^4$	<i>s-cis/s-trans</i>
Ph	H	H	Ph	2/98
H	H	H	H	10/90–60/40 <sup>a</sup>
$\text{CH}_3$	H	H	$\text{CH}_3$	36/64
$\text{C}_2\text{H}_5$	H	H	H	39/61
$\text{CH}_3$	H	H	H	42/58
H	$\text{CH}_3$	H	H	100/0
H	$\text{CH}_3$	$\text{CH}_3$	H	100/0
H	Ph	Ph	H	100/0
$\text{CH}_3$	$\text{CH}_3$	H	H	100/0
$\text{CH}_3$	H	$\text{CH}_3$	H	100/0

<sup>a</sup> Varied depending on the temperature.

mated to be  $>30 \text{ kcal/mol}$ .<sup>20</sup>

### The Electronic Structure

Pursuing an extended Hückel MO analysis of  $\text{Zr}$ -diene interactions in  $\text{ZrCp}_2(\text{C}_4\text{H}_6)$ , we have examined the electronic origins of the unique reactivity that the diene complexes of  $\text{Zr}$  exhibit.<sup>21</sup> In an attempt to compare the energies of the *s-cis* and *s-trans* isomers of  $\text{ZrCp}_2(\text{C}_4\text{H}_6)$ , each structure was optimized by choosing geometrical variables as defined to the right of the interaction diagrams in Figure 3. The calculated difference in energy between the two optimized structures was found to be slight, favoring the *s-cis* form by merely 0.07 eV, in harmony with experimental observation (*s-cis/s-trans* = 75/25<sup>9a</sup> or 55/45.<sup>6b</sup> In contrast, the total energy of a classical diene complex,  $\text{Fe}(\text{CO})_3(s\text{-cis}\text{-C}_4\text{H}_6)$ , is well below that of  $\text{Fe}(\text{CO})_3(s\text{-trans}\text{-C}_4\text{H}_6)$ . The difference amounts to 1.3 eV.

The analysis of the electronic structure of  $\text{ZrCp}_2(\text{C}_4\text{H}_6)$  in Figure 3 takes into account the frontier orbitals of a  $\text{ZrCp}_2$  fragment and the way in which they

(19) (a) Ziegler, M. L. *Z. Anorg. Chem.* **1972**, *392*, 173. (b) Sasse, H. E.; Ziegler, M. L. *Ibid.* **1972**, *392*, 167. (c) Guggolz, E.; Oberdorfer, F.; Ziegler, M. L. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36*, 1060. (d) Pierpont, C. G. *Inorg. Chem.* **1978**, *17*, 1976. (e) Tachikawa, M.; Shapley, J. R.; Haltiwanger, R. C.; Pierpont, C. G. *J. Am. Chem. Soc.* **1976**, *98*, 4561.

(20) (a) Kai, Y.; Kanehisa, N.; Miki, K.; Kasai, N.; Akita, M.; Yasuda, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3735. (b) Dorf, U.; Engel, K.; Erker, G. *Organometallics* **1982**, *2*, 462.

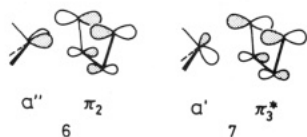
(21) Tatsumi, K.; Yasuda, H.; Nakamura, A. *Isr. J. Chem.* **1983**, *23*.

Table IV.  
Calculated Overlap Populations in  $\text{Fe}(\text{CO})_3(s\text{-cis-}C_4H_6)^a$ ,  
 $\text{ZrCp}_2(s\text{-cis-}C_4H_6)^b$  and  $\text{ZrCp}_2(s\text{-trans-}C_4H_6)^c$

	$(\text{CO})_3\text{Fe} \begin{array}{c} C_1 \\ \diagdown \\ C_2-C_3 \\ \diagup \\ C_4 \end{array}$	$\text{Cp}_2\text{Zr} \begin{array}{c} C_1 \\ \diagdown \\ C_2-C_3 \\ \diagup \\ C_4 \end{array}$	$\text{Cp}_2\text{Zr} \begin{array}{c} C_1 \\ \diagup \\ C_2 \\ \diagdown \\ C_3 \\ C_4 \end{array}$
M-C <sub>1</sub>	0.202	0.338	0.204
M-C <sub>2</sub>	0.184	0.060	0.164
C <sub>1</sub> -C <sub>2</sub>	0.979	0.991	1.007
C <sub>2</sub> -C <sub>3</sub>	0.974	1.012	0.946

<sup>a</sup> $L = 0.8 \text{ \AA}$ ,  $\theta = 15^\circ$ . <sup>b</sup> $L = 0.3 \text{ \AA}$ ;  $\theta = 30^\circ$ . <sup>c</sup> $\varphi = 15^\circ$ .

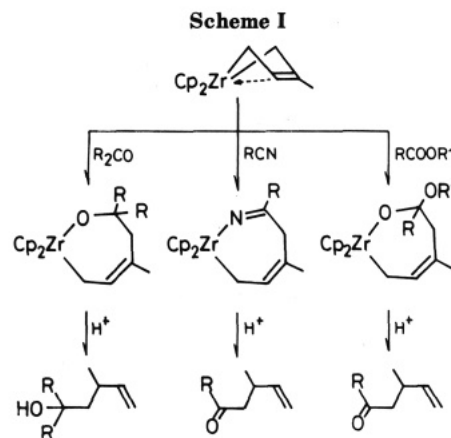
interact with  $\pi$ -type orbitals of *s-cis*- and *s-trans*-butadienes. In the middle of the interaction diagrams, there are five  $\text{ZrCp}_2$  orbitals. The three low-energy orbitals sit in the  $yz$  plane and will be used to form bonds with incoming diene ligands.<sup>22</sup> For the  $d^2$  electron configuration of  $\text{ZrCp}_2$ , only the lowest  $1a_1$  is doubly occupied. On the left side of Figure 3, the occupied  $\pi_2$  of *s-cis*- $C_4H_6$  finds a symmetry match with the unoccupied  $b_2$  of  $\text{ZrCp}_2$ , as it does with the  $a''$  (6) in  $\text{Fe}(\text{CO})_3(s\text{-cis-}C_4H_6)$ .<sup>23</sup> The so-called donation type of interaction is thus achieved. Back-donation occurs through  $1a_1-\pi_3^*$  mixing (7) of  $\text{Fe}(\text{CO})_3(s\text{-cis-}C_4H_6)$ . We attribute



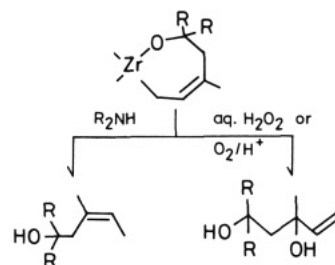
the weak  $1a_1-\pi_3^*$  interaction to a small orbital overlap,  $S = 0.117$ . The overlap integral of the analogous  $a'-\pi_3^*$  pair (7) of  $\text{Fe}(\text{CO})_3(s\text{-cis-}C_4H_6)$  is much stronger,  $S = 0.182$ . The two facts that the back-donation of electrons to  $\pi_3^*$  rises from the  $a_1$  symmetry orbital and that the interaction itself is not very strong are reasons for the unique facets of the Zr-diene bonding: comparable stability between the *s-cis* and *s-trans* isomers; strong  $1,4-\sigma$ -bond character in the *s-cis* complex; and resulting high reactivity toward electrophiles.

At the right of the diagrams in Figure 3, a major bonding interaction is indicated between  $\text{ZrCp}_2 b_2$  and *s-trans*- $C_4H_6 \pi_2$ . The  $\pi_2$  donates nearly the same amount of electrons (1.468 e) to  $\text{ZrCp}_2$  as *s-cis*  $\pi_2$  does (1.441 e). However, the most interesting feature of the diagram is that *s-trans*  $\pi_3^*$  is capable of interacting with  $1a_1$  of  $\text{ZrCp}_2$  to some extent, or at least to the same extent as *s-cis*  $\pi_3^*$ . In the case of  $\text{Fe}(\text{CO})_3(s\text{-trans-}C_4H_6)$ ,  $\pi_3^*$  was found to hardly overlap with either  $a'$  or  $a''$  of  $\text{Fe}(\text{CO})_3$ , while  $a'-\pi_3^*$  (*s-cis*) overlap was substantial as shown in 7. The lack of  $a'$  (or  $a''$ )- $\pi_3^*$  interactions is the reason why conjugated dienes avoid an *s-trans* conformation when they are coordinated to Fe. For  $\text{ZrCp}_2(C_4H_6)$ , on the other hand, the presence of a moderate  $1a_1-\pi_3^*$  interaction enables the *s-trans* complex to coexist with the *s-cis* isomer.

The overlap populations calculated for the optimized geometries of  $\text{Fe}(\text{CO})_3(s\text{-cis-}C_4H_6)$ ,  $\text{ZrCp}_2(s\text{-cis-}C_4H_6)$ , and  $\text{ZrCp}_2(s\text{-trans-}C_4H_6)$  aid us in deepening our understanding of metal-to-diene bonds. These are summarized in Table IV. In  $\text{Fe}(\text{CO})_3(s\text{-cis-}C_4H_6)$ , all carbon



Scheme II



atoms of butadiene are almost equally involved in the bond with Fe, and the  $C_1-C_2$  bond is as strong as the  $C_2-C_3$  bond. On the other hand,  $\text{ZrCp}_2(s\text{-cis-}C_4H_6)$  contains very strong  $\text{Zr}-C_1(C_4)$  bonds and concomitant weak  $\text{Zr}-C_2(C_3)$  interactions. As a consequence, the  $C_2-C_3$  bond assumes more double-bond character than the terminal  $C_1-C_2$  and  $C_3-C_4$  bonds. The notable  $1,4-\sigma$ -bond character in  $\text{ZrCp}_2(s\text{-cis-}1,3\text{-diene})$ , being derived from the above population analyses, occurs with the X-ray structure data given in Table I. Population analysis suggests that the best way of describing the bond between Zr and *s-cis*- $C_4H_6$  is structure 1.

For the *s-trans* complex  $\text{ZrCp}_2(s\text{-trans-}C_4H_6)$ , the inner carbons  $C_{2,3}$  participate significantly in  $\text{Zr}-C_4H_6$  bonding. The  $\text{Zr}-C_1(C_4)$  interactions are then not as strong as those of the *s-cis* complex. Perhaps a suitable bonding scheme of  $\text{ZrCp}_2(s\text{-trans-}C_4H_6)$  is 3, where the  $1,4-\sigma$ -bond nature is suppressed. This finding will be important when one considers the difference in reactivity between the *s-cis* and *s-trans* Zr complexes.

### Selective Addition to Carbonyl Compounds

One of the most important properties of diene complexes of early transition metals lies in their versatile reactivity toward both unsaturated hydrocarbons and polar electrophiles such as carbonyl compounds. Such dual character has never been observed for conventional organometallic compounds except for some allylic nickel complexes. This unusual feature is emphasized especially in the reaction of  $\text{ZrCp}_2(\text{isoprene})$  with saturated or unsaturated ketones, aldehydes, esters, and nitriles (Scheme I).<sup>24</sup> The complex readily reacts with these electrophiles under mild conditions ( $0-20^\circ\text{C}$ ) at the

(24) (a) Yasuda, H.; Kajihara, Y.; Mashima, K.; Nagasuna, K.; Nakamura, A. *Chem. Lett.* 1981, 671. (b) Kai, Y.; Kanehisa, N.; Miki, K.; Kasai, N.; Akita, M.; Yasuda, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* 1983, 56, 3735. (c) G. Erker, G.; Engel, K.; Atwood, J. L.; Hunter, W. E. *Angew. Chem. Int. Ed. Engl.* 1983, 22, 494. (d) Erker, G.; Dorf, U. *Ibid.* 1983, 22, 777. (e) Yasuda, A.; Nagasuna, K.; Asami, K.; Nakamura, A. *Chem. Lett.* 1983, 955.

(22) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* 1976, 98, 1729.

(23) (a) Tatsumi, K.; Fueno, T. *Bull. Chem. Soc. Jpn.* 1976, 49, 929.

(b) A theoretical analysis of  $\text{Mn}(C_4H_6)_2L$ ; Harlow, R. L.; Kusic, P. J.; McKinney, R. J.; Wreford, S. S. *Organometallics* 1982, 1, 1508.

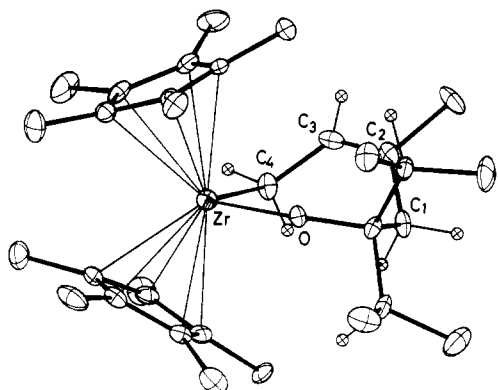
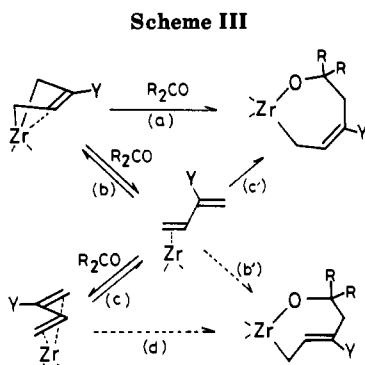
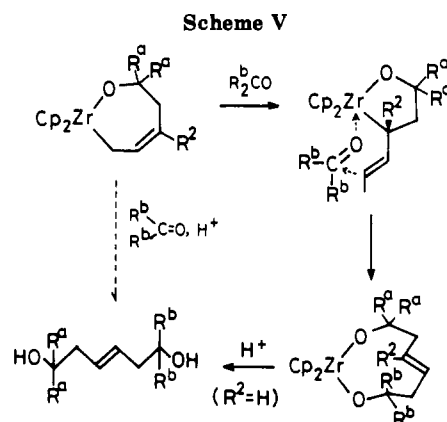
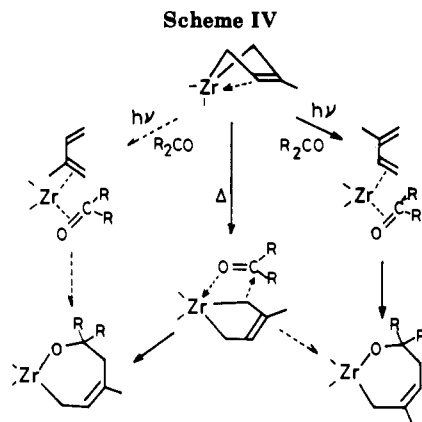


Figure 4. Structure of the compound obtained from 2,5-dimethyl-3-pentanone and  $\text{ZrCp}_2(\text{isoprene})$ .



sterically more hindered  $\text{C}_1$  atom of isoprene with extremely high regioselectivity (95–100%). Acidic cleavage of the inserted compounds generally produces a  $\gamma,\delta$ -unsaturated alcohol or ketone selectively (Scheme I), while the base-catalyzed cleavage gives a  $\beta,\gamma$ -unsaturated alcohol or ketone (Scheme II). When the ketone inserted complexes were oxidized with aqueous 30%  $\text{H}_2\text{O}_2$  or air followed by hydrolysis, diols were obtained in good yield.<sup>24e</sup> Thus the subtle electronic and environmental difference existing between  $\text{C}_1$  and  $\text{C}_4$  atoms of isoprene is amplified by complexation to zirconium to allow selective reaction. A four-centered insertion mechanism has been proposed for the regioselective reaction (see Scheme IV). The LUMO of  $\text{MCp}_2(\text{butadiene})$  has a shape similar to  $1a_1$  of  $\text{MCp}_2$  in Figure 3, so that the access of a carbonyl compound to the metal is restricted to occur from the direction of the  $y$  axis. The C–C bond formation occurs preferentially at the  $\text{C}_1$  atom, since the  $\text{C}_1$  atom is more negative than the  $\text{C}_4$  atom due to the inductive effect of the methyl group. The coplanar orbital arrangement does not allow the traditional six-membered transition state.

Two reaction pathways are conceivable for insertion of carbonyl compounds. One is insertion into the *s-trans*-diene complex, and the other is insertion into the *s-cis* isomer. In order to distinguish the two reaction pathways, reactions of  $\text{Zr}(\text{C}_5\text{Me}_5)_2(\text{butadiene})$  (100% *s-trans*) and  $\text{Zr}(\text{C}_5\text{Me}_5)_2(\text{isoprene})$  (100% *s-cis*) with 2,4-dimethyl-3-pentanone were examined. If the reaction proceeds with retention of configuration, each of the stereoisomers should give a different product according to process a or d (Scheme III). The X-ray analysis of the above two ketone-inserted products revealed that both products have essentially the same molecular structure of *Z* configuration (Figure 4).<sup>24b</sup> A similar structure has also been reported for the diphenyl



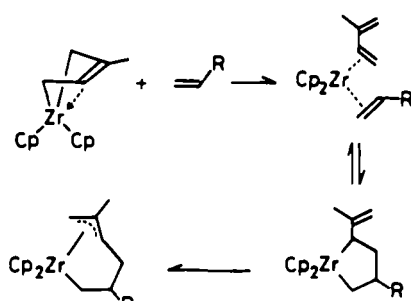
ketone adduct of  $\text{ZrCp}_2(\text{butadiene})$ .<sup>24c</sup> This indicates that the *s-trans*-butadiene complex reacts with a change in conformation (process  $c \rightarrow c'$  or  $c \rightarrow b \rightarrow a$ ), while the *s-cis* isomer reacts without a change in the geometry following the process a or b  $\rightarrow c'$ .

In contrast to the thermally induced insertion reactions, photoinduced reaction of ketones occurred preferentially (78%) at the sterically less crowded  $\text{C}_4$  atom at  $-70^\circ\text{C}$  (Scheme IV).<sup>24d</sup> The mode of insertion is in principle the same as the [2 + 2]-type oxidative coupling of alkenes or alkynes with  $\text{ZrCp}_2(\text{isoprene})$  described later.

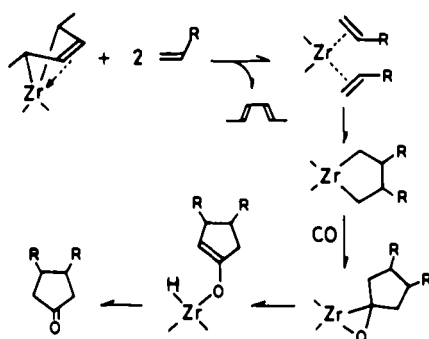
$\text{ZrCp}_2(\text{isoprene})$  and  $\text{ZrCp}_2(2,3\text{-dimethylbutadiene})$  react with only 1 equiv of ketones, aldehydes, or nitriles, even in the presence of excess substrates at high temperature, while  $\text{ZrCp}_2(\text{butadiene})$ ,  $\text{ZrCp}_2(1,3\text{-pentadiene})$ , and  $\text{ZrCp}_2(2,4\text{-hexadiene})$  readily react with 2 equiv of 3-pentanone, isobutanol, or pivalonitrile at ambient temperature on both ends of the diene ligand to give derivatives of 3-hexene-1,6-diols or -1,6-diones through hydrolysis.<sup>11,25</sup> Thus alkyl substitution at  $\text{C}_2$  and/or  $\text{C}_3$  atoms of a butadiene unit inhibits the double insertion of carbonyl compounds, presumably due to the difficulty in forming the five-membered intermediate which involves a sterically unfavorable tertiary  $\alpha$ -carbon (Scheme V where  $\text{R}^2 = \text{CH}_3$ ). In the case of butadiene, 1,3-pentadiene, and 2,4-hexadiene complexes, the initially formed seven-membered oxametallacycle equilibrates with the corresponding five-membered oxametallacycle, since it involves no tertiary  $\alpha$ -carbon atom in the ring; i.e.,  $\text{R}^2 = \text{H}$ . The five-membered intermediate containing an allylmetal group may react with a ketone at its  $\gamma$ -position via a six-membered transition

(25) Asami, K.; Yasuda, H.; Nakamura, A. 47th National Meeting. Chemical Society Japan, Kyoto, 1982; Abstr 4G25.

Scheme VI



Scheme VII



state to give the (*E*)-3-hexene-1,6-diol skeleton. This process agrees well with that proposed for the three-selective addition of aldehydes to allylic zirconium compounds.<sup>26</sup> The above double-insertion sequence is also effective for the introduction of two different carbonyl compounds into the diene termini (Scheme V). For example, the 1:1 reaction of  $ZrCp_2$ (butadiene) with 3-pentanone followed by the addition of isobutanal gave 3-ethyl-8-methyl-5-nonene-3,8-diol in >95% yield on hydrolysis.

The use of  $Ti(OR)_4$  or  $TiCl_2(OR)_2$  ( $R = CH_3, C_2H_5, C_3H_7, C_4H_9$ , etc.) in place of  $ZrCp_2Cl_2$  provides a facile method to perform the corresponding single- or double-insertion reactions in large scale since these reagents are readily available at low cost.<sup>25</sup>

$TaCp$ (butadiene)<sub>2</sub> also reacts with 4 equiv of aliphatic ketone at 0–30 °C to give upon hydrolysis the derivatives of 3-hexene-1,6-diol, but  $TaCp$ (isoprene)<sub>2</sub> reacts with only 2 equiv of ketone to give derivatives of 3-penten-1-ol. The mode of insertion compares closely to that observed for zirconium–diene complexes.<sup>3</sup>

### Oxidative Coupling of Unsaturated Hydrocarbons

Most 1-alkenes (1-butene, 1-octene, etc.) readily react with  $ZrCp_2$ (diene) at ambient temperature to give the 1:1 adduct containing one  $\sigma$ - and one  $\eta^3$ -allyl  $M-C$  bonds.<sup>27,28</sup> When the isoprene complex is used, the C–C bond formation takes place selectively at the sterically less congested  $C_4$  atom of isoprene through the [2 + 2]-type oxidative coupling process.<sup>28</sup> Thus, the bonding site greatly differs from that observed in the thermally induced insertion of carbonyl compounds (Scheme VI).

(26) (a) Yamamoto, Y.; Maruyama, K. *Tetrahedron Lett.* 1981, 2895. (b) Mashima, K.; Yasuda, H.; Asami, K.; Nakamura, A. *Chem. Lett.* 1983, 219.

(27) (a) Yasuda, H.; Kajihara, Y.; Nagasuna, K.; Mashima, K.; Nakamura, A. *Chem. Lett.* 1980, 719. (b) Erker, G.; Engle, K.; Dorf, U.; Atwood, J. L.; Hunter, W. E. *Angew. Chem., Int. Ed. Engl.* 1982, 21, 914.

(28) Kai, Y.; Kanehisa, N.; Miki, K.; Kasai, N.; Mashima, K.; Nagasuna, K.; Yasuda, H.; Nakamura, A. *Chem. Lett.* 1982, 1979.

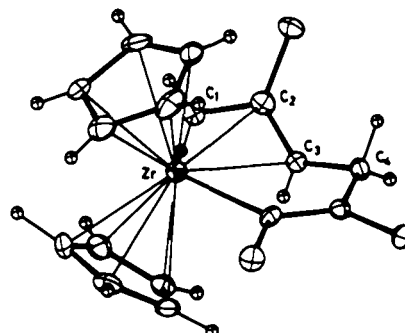
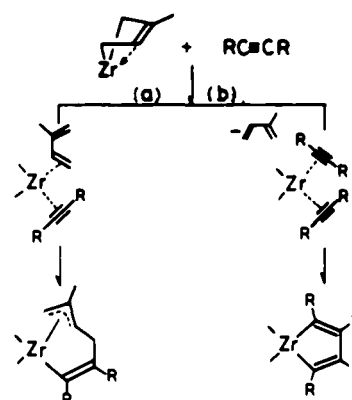


Figure 5. Structure of the addition product prepared from 2-butyne and  $ZrCp_2$ (isoprene).

Scheme VIII



The 2,4-hexadiene ligand was found to be among the most weakly bonded ligands to zirconium and was easily expelled at ordinary temperatures by the addition of 2–3 equiv of 1-alkenes to give 3,4-dialkylzirconacyclopentanes by oxidative coupling of 1-alkenes.<sup>11b</sup> Analogous oxidative coupling has been found in the reaction of  $Ti(C_6Me_6)_2(C_2H_4)$  with ethylene.<sup>29</sup> From a synthetic point of view, a variety of 3,4-disubstituted cyclopentanones were prepared in 70–80% yield by treating the complex with 1-alkenes followed by CO bubbling and hydrolysis (Scheme VII). The reaction may proceed through a zirconium enolate as reported for the insertion of CO into nonsubstituted zirconacyclopentane.<sup>30</sup> 1,4-Diphenylbutadiene and 2,3-dimethylbutadiene bind strongly to zirconium, and therefore alkenes are inert toward these complexes. The relative strength of dienes in coordination to metals was estimated to be in the following order as confirmed by the ligand exchange reactions: 1,4-diphenylbutadiene > 2,3-dimethylbutadiene > isoprene  $\approx$  butadiene > 1,3-pentadiene > 2,4-hexadiene.

A variety of alkynes also react with  $Zr(C_5R_6)_2$ (diene) ( $R = H$  or  $CH_3$ ) in essentially the same manner as described for the addition reaction of 1-alkenes.<sup>11,27</sup> Mono- and dialkyl-substituted acetylenes commonly perform the 1:1 addition reaction (path a in Scheme VIII). As a typical example, the X-ray structure of the 2-butyne inserted product obtained from  $ZrCp_2$ (isoprene) and 2-butyne is shown in Figure 5.<sup>28</sup> Our result verified the proposed structure of an active species for Fe(II)- or Ni(O)-catalyzed codimerization of a diene with an alkyne.<sup>31</sup> When aryl-substituted acetylene was used, the

(29) Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* 1983, 105, 1136.

(30) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* 1978, 100, 2716.

reaction involved the elimination of the diene, followed by oxidative coupling of alkynes, to give zirconacyclopentadiene derivatives (path b). Systematic ligand exchange experiments confirm that the strength of coordination to Zr increases in the following order which parallels their  $\pi$ -acidity:  $\text{PhC}\equiv\text{CPh} > \text{PhC}\equiv\text{CH} > \text{CH}\equiv\text{CH} > \text{C}_2\text{H}_5\text{C}\equiv\text{CH} \approx \text{C}_4\text{H}_9\text{C}\equiv\text{CH}$ . Therefore, in the reaction between the labile 2,4-hexadiene complex and  $\text{PhC}\equiv\text{CPh}$ , the ligands readily exchanged and gave 2,3,4,5-tetraphenylzirconacyclo-2,4-pentadiene, while  $\text{ZrCp}_2(1,4\text{-diphenylbutadiene})$  was unreactive toward 1-butyne or 1-hexyne. Thus, an appropriate combination between dienes and alkynes is required to obtain their 1:1 addition product in good yield.

The relative reactivity of various substrates toward  $\text{Cp}_2\text{Zr}(\text{isoprene})$  was estimated to be in the following

(31) (a) Carbonaro, A.; Greco, A.; Dall'Asta, G. *J. Org. Chem.* **1968**, *33*, 3948. (b) Heimbach, P.; Ploner, K.; Thömel, F. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 276.

(32) Churchill M. R.; Young, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 6462.

(33) The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

order on the basis of competitive reactions: ketone > aldehyde > ester > alkyne > diene > alkene.

### Concluding Remarks

The significant features of early-transition-metal-diene complexes found to date are (1) a variety of new synthetic approaches, (2) s-trans coordination, (3) a bent metallacyclo-3-pentene structure for s-cis coordination, (4) the regioselective addition of unsaturated hetero compounds, and (5) [2 + 2] type of oxidative coupling of olefins, dienes, and alkynes to many new metallocycles and to catalysis for oligomerization. Future research will surely find further new developments in the organometallic chemistry of the early transition metals.

*Thanks are due to our productive and stimulating coworkers, whose names are given in the references. We are indebted to Prof. N. Kasai and Dr. Y. Kai of Osaka University for the X-ray work including unpublished data. Special thanks also go to Prof. G. Erker of the Max Planck Institute for sending us several manuscripts prior to publication and to Dr. W. E. Rhine of University of Dayton Research Institute for suggestions regarding the manuscript. This work was supported partially by a Grant-in-Aid for Special Project Research (No. 57218014) from the Ministry of Education, Science and Culture, Japan.*