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Adaptable coordination modes of conjugated 1,3-diene: uniqueness of *s-trans* coordination

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Dedicated to Professor P. Royo for his continuous contributions in Inorganic and Organometallic Chemistry

Abstract

We briefly describe the unique coordination mode of *s-trans*-1,3-diene complexes in this review. Since the first discovery of mononuclear *s-trans*-1,3-diene complexes of zirconocene and hafnocene, this unique coordination mode has been found for a wide variety of transition metals over the Periodic Table. Herein we summarize general aspects of the mononuclear *s-trans* diene complexes including the recent results, and also describe dinuclear and multinuclear complexes that coordinate in an *s-trans* fashion to polyenes.

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Keywords: Adaptable coordination modes; Conjugated 1,3-diene; *s-trans* Coordination

1. Introduction

Conjugated dienes have been found to coordinate to almost all metal atoms or ions throughout the Periodic Table. The remarkable propensity of the diene ligands to coordinate in different coordination modes to metals is apparently attributed to their adaptability and flexibility. Recent results of organometallic research in this area have revealed various diene–metal bonding stereochemistries depending crucially on the metal and the ancillary ligands [1,2]. Typical examples of the diene

coordination modes for mononuclear and dinuclear complexes are schematically illustrated in Fig. 1.

Among the 1,3-diene complexes having *s-cis* mode, a metallacyclic bonding nature has been realized for the heavier early transition metals such as Hf and Ta; these complexes are best formulated according to mode **B** (Fig. 1). In the case of lanthanides and actinides, the metallacyclic nature of the diene–metal bonding is much more enhanced and thus highly ionic metal–carbon bonding is presumed for $\text{Cp}_2^*\text{Ac}(s\text{-cis-}\eta^4\text{-1,3-butadiene})$ (**1**) (Ac = Th and U) [3–5]. The diene also forms complexes of main group metals with some degree of ionic bonding character. Group 2 metals such as Mg, Ca, and Sr give the 1:1 diene complexes $\text{M}(1,3\text{-diene})(\text{thf})_n$ (**2**: M = Mg, 1,3-diene = 1,4-diphenyl-1,3-butadiene, $n = 3$; **3**: M = Ca, 1,3-diene = 1,4-diphenyl-2,3-dimethyl-1,3-butadiene, $n = 4$; **4**: M = Sr, 1,3-

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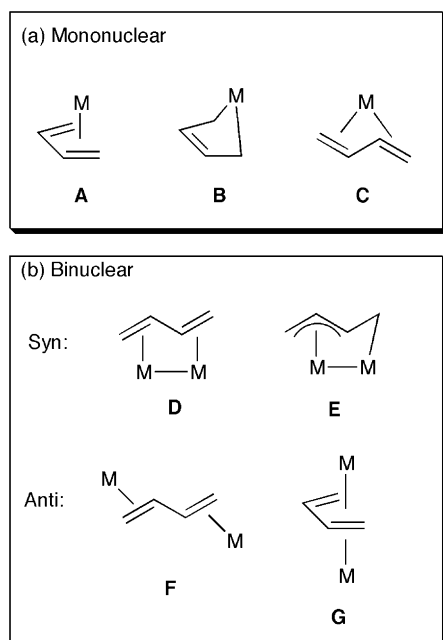
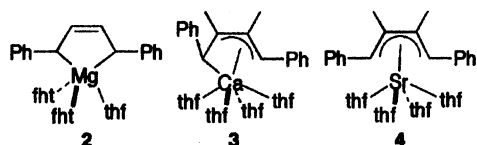


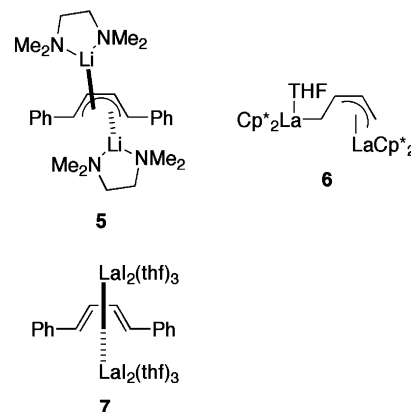
Fig. 1. Some typical coordination modes observed for (a) mononuclear and (b) dinuclear η^4 -1,3-diene complexes.

diene = 1,4-diphenyl-2,3-dimethyl-1,3-butadiene, $n = 4$) with differing degree of ionicity at the metal–diene bonds [6,7]. Some of these diene complexes, particularly ones with unsubstituted diene, are so reactive as to insert other molecules of the same diene to give oligomers and polymers depending on the conditions [8,9].



The versatility and adaptability of the diene ligand are owing to its wide formal ionic charge spanning from 0 to -2 . The formally neutral diene ligand makes a strong π -bond with zero-valent late transition metals such as Fe in $(\eta^4$ -1,3-diene)Fe(CO)₃ and so on (mode A, Fig. 1), whereas another canonical form is the dianionic 6π system that coordinates to dicationic metal ions, e.g. Mg(diene) adducts and so on. A similar adaptable character of carbon ligands has already been observed for cyclopentadienyl (= Cp) and cyclooctatetraene (= COT) ligands, which form strong bonds with almost all the metals. The Cp–M bonding of main-group elements is polarized as $\text{Cp}^- \text{M}^+$, to some extent, reflecting the stability of the 6π -electronic carbocycle. In the case of Group 1 elements, bilateral coordination of the Cp ligand has been observed and hence this bridging ligation generates an ionic $[\text{CpM}]_n$ chain structure. Similar bilateral coordination of 1,3-butadiene and its derivative (mode G, Fig. 1) was observed in the case of dinuclear diene complexes of Li, Li(TMEDA)(η^3 : η^3 -*s*-

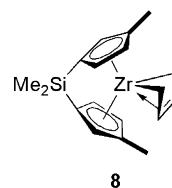
cis-PhCH=CHCH=CHPh)Li(TMEDA) (5) [10], and La, Cp₂La(η^1 : η^3 -1,3-butadiene)LaCp₂ (6) [11] and LaI₂(THF)₃(η^4 : η^4 -*s*-*cis*-PhCH=CHCH=CHPh)LaI₂(THF)₃ (7) [12], all of which have *s*-*cis*-1,3-diene structure suitable for the 6π dianionic carbocycles.



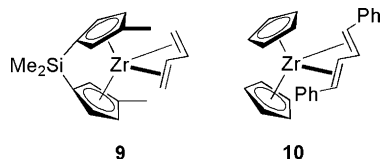
One of the most interesting coordination modes of 1,3-diene is a mononuclear *s*-*trans*-1,3-diene complex (mode C, Fig. 1), which was found for the first time for the zirconocene fragment ‘Cp₂Zr’, and now found not only for early transition metals (Zr, Hf, Nb, Ta, Mo, W, and Re) but also for late transition metal (Ru). In this review, we briefly describe the structural preference and bonding nature of the mononuclear *s*-*trans*-1,3-diene complexes together with dinuclear and multi-nuclear complexes.

2. Bonding nature of *s*-*trans* coordination mode of 1,3-diene ligand bound to zirconium and hafnium as revealed by physical data

The stereochemistry of the 1,3-diene complexes of zirconocene in solution is readily determined by NMR spectroscopy, which gives not only static information from chemical shifts and coupling constants in ¹H- and ¹³C-NMR spectra, but also dynamic information (rapid equilibria among the possible stereo isomers) due to the fluxional behavior in temperature-variant NMR spectra. In particular, autotropic ligand-flipping equilibria (“envelope-flip” or topoisomerization) have been observed for the *s*-*cis*-1,3-diene complexes of zirconocene [13,14]. A recent example is the *s*-*cis* isomer of *ansa*-Me₂Si(C₅H₃Me)₂Zr(*s*-*cis*- η^4 -1,3-butadiene) (8), giving rise to the activation energy of 13.5–13.7 kcal mol⁻¹ [15].



The proton–proton coupling constants as well as the chemical shift values provide information about the *s-cis*- and *s-trans*-1,3-diene modes, which can be definitely distinguished by the comparison of the chemical shift values of the *s-trans*-1,3-diene complexes with those found for the corresponding *s-cis*-1,3-diene complexes. Especially, the $C^2H^2-C^3H^3$ coupling constant of the 1,3-diene moiety directly reveals the conformation preference: values such as ~ 10.7 Hz are found for *s-cis* and 15.0–15.8 Hz for *s-trans* by computer simulation of the pattern assignable to the equivalent protons [16]. It is noteworthy that the value for the *s-trans* is larger than that of free 1,3-butadiene. The ^{13}C -NMR chemical shifts at the terminal carbons of *s-cis* and *s-trans* are quite different and serve as a diagnostic tool. The values of the terminal carbons for *ansa*- $Me_2Si(C_5H_3Me)_2Zr(s-cis-\eta^4-1,3-butadiene)$ (**8**) are 51.4 and 50.6 ppm (two terminal carbons are not magnetically equivalent in the *s-cis* case) and those for *ansa*- $Me_2Si(C_5H_3Me)_2Zr(s-trans-\eta^4-1,3-butadiene)$ (**9**) are 59.6 ppm (major isomer) and 62.8 ppm (minor isomer) (two isomers are possible but terminal carbons in each isomer are symmetry equivalent) [15]. The former two values indicate the sp^3 hybridized carbons as expected from metallacyclic nature of the bonding in *s-cis*-1,3-diene ligation.



The structures of the *s-trans*-1,3-diene complexes of transition metals have been determined by the X-ray analysis and structural parameters are summarized in Table 1. Among them, the metrical values of two *s-trans*-1,3-diene complexes of zirconium, **9** [15] and

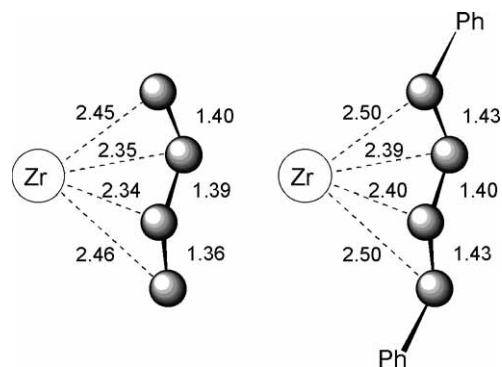


Fig. 2. Metrical values (Å) of the *s-trans*-1,3-diene complexes of zirconium; *ansa*- $Me_2Si(C_5H_3Me)_2Zr(1,3-butadiene)$ (**9**) [15] and $Cp_2Zr(1,4-diphenyl-1,3-butadiene)$ (**10**) [17].

$Cp_2Zr(s-trans-\eta^4-1,4-diphenyl-1,3-butadiene)$ (**10**) [17] are schematically illustrated in Fig. 2, indicating almost the same C–C bond lengths within C_{1-4} in sharp contrast to the long–short–long alternation observed in *s-cis*-1,3-diene complexes of zirconocene. The Zr– C_{1-4} bond lengths indicate shorter Zr–C at the central diene carbons, 2.34–2.40 Å, compared with Zr–C at the outer carbons, 2.45–2.50 Å. A considerable bonding is thus expected for each of the two central carbons to the Zr center. The observed torsion angle (124° for **9** and 126° for **10**) shows that the diene is wrapping the metal by folding the originally planar butadiene moiety, indicating that the *s-trans* butadiene ligand seems to be much π -donative to the metal and hence the *s-trans*-1,3-diene coordinates to the metal as the π^2 -mode. Accordingly, the proton NMR shift values of the Cp ligands are observed at higher field compared with the corresponding values of the *s-cis* isomer (Table 2).

The observed higher reactivity of the *s-trans*-1,3-diene ligand of zirconocene upon thermal excitation has

Table 1
Structural parameters for some mononuclear *s-trans*-1,3-diene complexes of transition metals

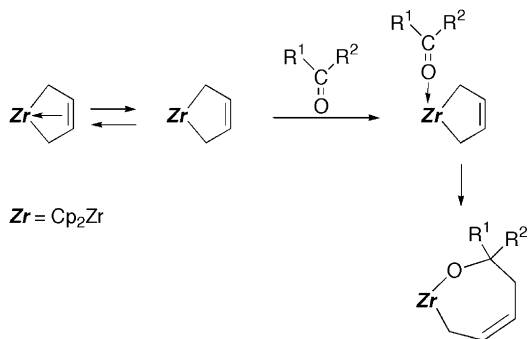
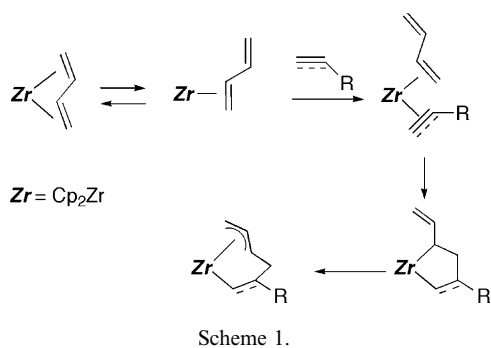
Complex	M–C(1), M–C(4)	M–C(2), M–C(3)	C(1)–C(2), C(3)–C(4)	C(2)–C(3)	Torsion angle of the diene unit	Ref.
9	2.453(3), 2.455(3)	2.352(3), 2.338(3)	1.402(5), 1.364(6)	1.393(5)	124.3(4)	[15]
10 ^a	2.51(1) [2.49(1)], 2.51(1) [2.51(1)]	2.391(1) [2.36(1)], 2.40(1) [2.38(1)]	1.44(2) [1.38(2)], 1.40(2) [1.38(2)]	1.42(2) [1.45(2)]	126.8 [125.5]	[17]
14	2.42(2), 2.30(2)	2.31(2), 2.31(1)	1.32(3), 1.33(3)	1.53(4)	–	[28]
15	2.264(7), 2.29(4)	2.20(3), 2.30(4)	1.39(2), 1.29(3)	1.40(2)	–	[31]
17 (Diene = 2,5-dimethyl-2,4-hexadiene)	2.390(3), 2.365(3)	2.209(3), 2.234(3)	1.418(4), 1.401(4)	1.408(4)	–	[34]
23 (Diene = 2,4-dimethyl-1,3-pentadiene)	2.196(3), 2.291(3)	2.146(3), 2.107(3)	1.392(4), 1.402(4)	1.457(4)	122.6	[48]
23 (Diene = 2,5-dimethyl-2,4-hexadiene)	2.255(4), 2.278(5)	2.091(4), 2.089(4)	1.391(7), 1.399(7)	1.421(6)	123	[49]
24	2.256(3)	2.142(3)	1.450(8)	1.297(5)	114.2(6)	[50]
24 (Diene = 2,4-hexadiene)	2.306(3)	2.153(3)	1.372(5)	1.447(7)	125.4(7)	[50]
25 ^a	2.27(2) [2.27(2)], 2.23(4) [2.28(3)]	2.15(3) [2.09(3)], 2.10(3) [2.09(3)]	1.24(4) [1.31(4)], 1.29(4) [1.36(4)]	1.32(4) [1.17(4)]	–	[51]

^a Data in parentheses are the second molecule because complex **10** crystallized as two crystallographically independent molecules.

Table 2
Proton NMR chemical shifts of the Cp ligand in some 1,3-diene complexes, $\text{Cp}_2\text{M}(\text{diene})$ ($\text{M} = \text{Zr}$ and Hf) [16]

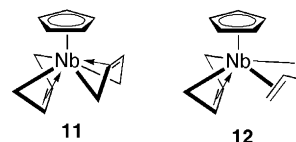
Stereochemistry	Dienes	Metal	Chemical shift (ppm)
<i>s-cis</i>	1,3-Butadiene	Zr	5.25
	Isoprene	Zr	5.28
	2,3-Dimethyl-1,3-butadiene	Zr	5.31
	1,3-Butadiene	Hf	5.23
	Isoprene	Hf	5.27
	2,3-Dimethylbutadiene	Hf	5.36
	1,4-Diphenyl-1,3-butadiene	Hf	4.84
<i>s-trans</i>			5.35
	1,3-Butadiene	Zr	4.92
	1,4-Diphenyl-1,3-butadiene	Zr	4.89
	1,4-Diphenyl-1,3-butadiene	Hf	4.88

indicated much higher population of the 16-electronic η^2 -diene species, which readily reacts with a variety of 2-electron donors such as alkenes, acetylenes, and so on (Scheme 1) [18,19]. In the case of the *s-cis*-1,3-diene complexes of zirconocene, thermal excitation gives a terminally bonded 16-electronic zirconium species (zircononacyclo-3-pentene), which is reactive to hetero-2-electron donors such as aldehydes, ketones, nitriles, and so on to give insertion compounds (Scheme 2) [20,21].



3. The electronic factors of the metal complex fragment suitable for *s-trans*-1,3-diene coordination mode

Since the unexpected discovery of *s-trans*-1,3-diene coordination in 1980, the rationale for the preference of *s-trans* coordination was sought [13,14,22]. The nature of bonding was first analyzed by the EHMO calculation and a preference of the *s-trans* mode was found for the terminally alkyl- or aryl-substituted dienes as the ligand [23,24]. The theoretical calculation indicated an apparent preference of this mode by the early transition metals. The preference of ' Cp_2Zr ' and its isoelectronic ' $\text{Cp}(\eta^4\text{-1,3-diene})\text{Nb}$ ' moiety over the corresponding Hf and Ta analogs was stressed. In the case of $\text{CpNb}(\textit{s-cis}\text{-}\eta^4\text{-1,3-diene})$ as the metal fragment, the coordination of the other diene takes place to give an *s-cis* and *s-trans* mixture, i.e. $\text{CpNb}(\textit{s-cis}\text{-}\eta^4\text{-1,3-diene})_2$ (**11**) and $\text{CpNb}(\textit{s-cis}\text{-}\eta^4\text{-1,3-diene})(\textit{s-trans}\text{-}\eta^4\text{-1,3-diene})$ (**12**) [25]. When Cp^* is used in place of Cp, no *s-trans* complex has been obtained [25], consistent with the same tendency observed for the zirconocene derivative. This is explained by the higher metal electron density in the presence of the Cp^* ligand [26]. When 1,3,7,9-decatetraene coordinates to the CpNb fragment, a similar $(\textit{s-cis}\text{-}\eta^4\text{-1,3-diene})(\textit{s-trans}\text{-}\eta^4\text{-1,3-diene})$ isomer, $\text{CpNb}(\eta^8\text{-C}_{14}\text{H}_{22})$ (**13**) results [27]. This unique bis-1,3-diene complex **13** is the product of homocoupling of 2,4-dimethylpentadienylpotassium caused by CpNbCl_4 .



The combination of co-ligands in the metal fragment is important for the *s-trans* preference. It is recently reported that 1,3-butadiene coordinates to a cationic Cp_2Ta fragment to give $[\text{Cp}_2\text{Ta}(\textit{s-trans}\text{-}\eta^4\text{-1,3-butadiene})]^+$ (**14**), which adopts the *s-trans* conformation predominantly and exhibits high reactivity quite similar to that of $\text{Cp}_2\text{Zr}(\textit{s-trans}\text{-}\eta^4\text{-1,3-butadiene})$ [28–30]. This similarity is thought to be caused by the electron-accepting nature of the 14-e $[\text{Cp}_2\text{Ta}]^+$ fragment. Furthermore, a similar preference of the *s-trans* mode has been found for isoelectronic Mo complexes such as $\text{CpMo}(\eta^3\text{-allyl})(\eta^4\text{-1,3-diene})$ (**15**) [31,32], $[\text{CpMo}(\eta^4\text{-1,3-diene})_2]^+$ (**16**) [32,33], $\text{CpMo}(\eta^4\text{-1,3-diene})(\text{NO})$ (**17**) [34,35], and $[\text{CpMo}(\text{CO})_2(\eta^4\text{-1,3-diene})]^+$ (**18**) [36–39], whereas the W analogs are thermally unstable and $\text{Cp}^*\text{W}(\text{NO})(\eta^4\text{-1,3-diene})$ (**19**) [40] and $[\text{CpW}(\text{CO})_2(\eta^4\text{-1,3-diene})]^+$ (**20**) [41,42] have been characterized spectroscopically at low temperature, and also for the isoelectronic Re complex $\text{Cp}^*\text{ReCl}_2(\eta^4\text{-1,3-diene})$ (**21**) [43]. It is again notable that the *s-trans*-1,3-diene complex **17** reacts with acetone and acetylene

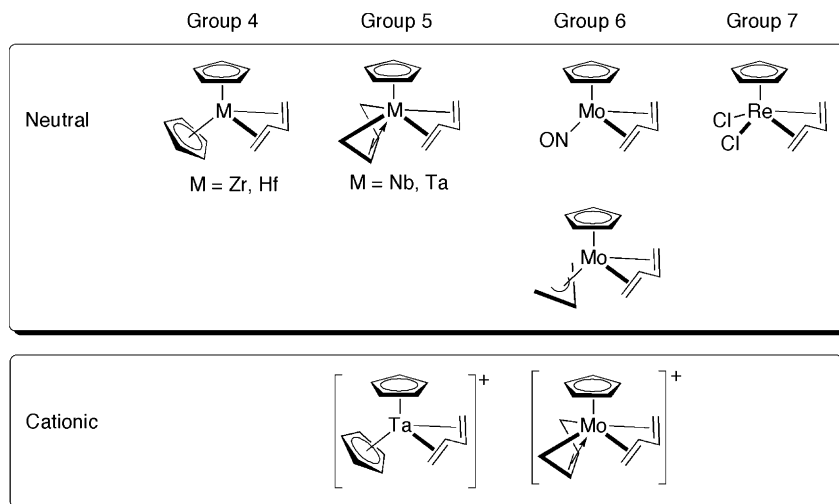


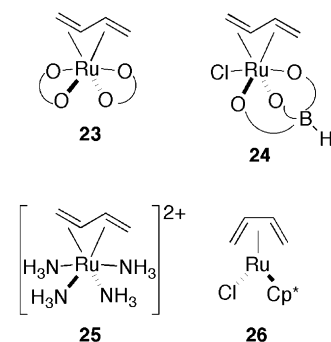
Fig. 3. Isoelectronic *s-trans*-1,3-diene complexes of early transition metals.

in a similar manner to zirconocene and cationic tantalocene derivatives as mentioned above to give the inserted product [44,45]. The involvement of one boron atom in the Cp ligand causes a stabilization of the *s-trans* complex Cp*[C₄H₄BN(CHMe₂)₂]Ta(*s-trans*-η⁴-1,3-butadiene) (**22**), probably by the electronic effect due to electron-withdrawing boron atom [46] (Fig. 3).

The precise bond lengths and angles of genuine *s-trans* 1,3-butadiene ligand remained to be elucidated because the size similarity between the *s-cis* and the *s-trans* isomers result in the formation of disordered. This tendency has been especially observed for the case of NbCp(η⁴-1,3-butadiene)₂ complex, where both bis(*s-cis*) and (*s-cis*)(*s-trans*) isomers **11** and **12** exist in the same crystal [25,47]. As shown in Fig. 2, an SiMe₂-bridged *ansa*-zirconocene **9** enables a precise determination of the *s-trans*-1,3-butadiene ligation by X-ray analysis owing to the separation of the diastereoisomers by crystallization [15], though the crystal structure of the butadiene complex of the simple zirconocene did not clearly confirm the *s-trans* conformation due to the large thermal motions of the two central carbon atoms [22]. The structure of the simple 1,3-butadiene complex of Ta has the same difficulty due to the large thermal motions (Table 1), which prevents the precise description of the *s-trans*-1,3-diene conformation, while the problem of Mo–diene complex is due to disorder.

Some ruthenium(II)–diene complexes such as Ru(acac)₂(η⁴-1,3-diene) (**23**) [48,49], TpRuCl(η⁴-1,3-diene) (**24**) [50], and [Ru(NH₃)₄(η⁴-1,3-diene)]²⁺ (**25**) [51] prefer the *s-trans* mode, in contrast to RuCp*Cl(η⁴-1,3-diene) (**26**), which prefers the *s-cis* mode [52]. This preference can now be explained by the large electronegativity difference estimated for the coordinating ligand atoms. The electronic deficiency around the ruthenium atom of the ‘Ru(acac)₂’, ‘TpRuCl’, and ‘[Ru(NH₃)₄]⁺’ fragments, as compared with the

‘RuCp*Cl’ fragment, may be compensated by the electron donating ability of the *s-trans* diene ligand. In addition to this electronic influence of the co-ligands, the overall stereochemistry at the Ru center seems to be influential for the preference of *s-cis* versus *s-trans* coordination mode. Since the *s-trans*-1,3-diene moiety may be regarded as a bidentate chelate, the Ru(II) center is approximated as a hexa-coordinated Oh structure with a d⁶ count. In the case of the *s-cis* coordination, the deviation from the regular Oh structure is enlarged even when the Cp ligand is regarded as a tridentate ligand. Thus, a combination of Cp and *s-cis*-1,3-diene may be regarded as a wedged “nor-metallocene (17 e-count)”, which thus takes a chloro ligand, e.g. C₅H₅(C₄H₆)MCl.



4. The steric factors preferring the *s-trans* diene coordination mode

The substituents on the 1,3-diene ligand play a crucial role for determining the *s-cis*/*s-trans* preference. The *s-trans* conformation requires a wider coordination environment especially suitable for the π-back donation from the metal. A plausible estimate of this widening amounts to 29% in the C₁–C₄ length relative to the *s-cis*

counter part, and hence the bite angle C_1-M-C_4 of the *s-trans*-1,3-diene is larger than that of the *s-cis*-1,3-diene. From comparisons within the same groups, e.g. $Cp_2M(\eta^4-1,3\text{-diene})$ ($M = Zr$ and Hf) and $CpM(\eta^4-1,3\text{-diene})_2$ ($M = Nb$ and Ta), it results that the complexes with heavier metals have a much higher tendency to adopt the *s-cis* mode and the second row transition metals actually take the *s-trans* coordination mode. For example, $Cp_2Hf(1,4\text{-diphenyl-1,3-butadiene})$ (**27**) prefers *s-cis* mode (ca. 75%), but the zirconium analog **10** is almost exclusively *s-trans*. These results are rather curious, if one invokes only a steric control, because the third transition metals have almost the same atomic radii as the corresponding second row metals, but these are the consequence of the well-known greater stability of metal–carbon σ -bonding for the third row transition metals and hence the 1,4-di- σ -bonding predominates in the *s-cis* mode for these heavier early transition metals.

From the early experiments, the Cp_2Zr fragment is known to give a mixture of *s-cis*- and *s-trans*-1,3-diene complexes, the ratio depending on the synthetic conditions. The preparation with the magnesium butadiene reagent in THF at low temperature affords the *s-cis* isomer in excess [16]. The other photochemical method starting from Cp_2ZrPh_2 was found to give the *s-trans* isomer as the major product [22]. The enthalpic difference between the *s-cis* isomers was evaluated by the thermal equilibrium in solution yielding 13.5–13.7 kcal mol⁻¹ at 278 K. A preference for the *s-trans* isomer was found in the *ansa*-type zirconocene fragments as described above. This may be understood by the expanded vacant metal d_π -orbital responsible to the π -donation of the butadiene orbital in the *s-trans* conformation (Fig. 4).

The substitution mode of the coordinating diene is very important for the bonding preference. Thus, dienes terminally substituted by alkyl groups have a remarkable trend to prefer the *s-trans* coordination mode. For example, ruthenium complexes having Cp^* and Cl ligands also favor the *s-trans* mode [52]. Terminal aryl substitution also preferably gives the *s-trans* isomer, for example the complex **10** is obtained dominantly as the *s-trans* isomer, which can be rationalized by the organometallic conjugation enhanced by the terminal aryl substituents. In contrast, the internal alkyl substitution

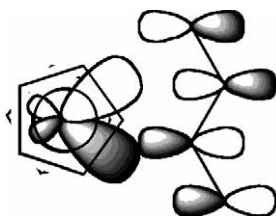
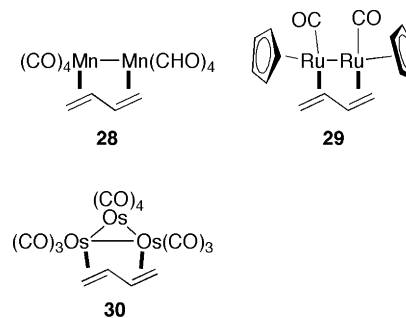


Fig. 4. Schematic drawing of donative interaction from the filled diene orbital to the Zr d-orbital in the *s-trans*-1,3-butadiene complex of zirconocene.

results in the *s-cis* coordination. The X-ray analysis of the 2,3-dimethyl-1,3-butadiene zirconocene complex clearly indicates the presence of metallacyclo-3-pentene structure for the *s-cis* isomers [22]. The thermodynamic stability of the terminal di-anionic 1,3-butadiene structure (mode **B**, Fig. 1) is enhanced by the alkyl substituent(s) on the central carbon atoms.

5. Dinuclear and multinuclear complexes of dienes and polyenes

Conjugated diene ligands have previously been reported to coordinate in an *s-trans* fashion to $M-M$ units (mode **D**, Fig. 1): some examples are carbonyl cluster complexes such as $Mn_2(CO)_8(s\text{-trans-}\eta^2:\eta^2\text{-1,3-butadiene})$ (**28**) [53], $Ru_2(CO)_2Cp_2(s\text{-trans-}\eta^2:\eta^2\text{-1,3-butadiene})$ (**29**) [54], and $Os_3(CO)_{10}(s\text{-trans-}\eta^2:\eta^2\text{-1,3-butadiene})$ (**30**) [55,56]. Dinuclear complexes of Cu(I), $[Cu(PPh_3)(OTf)]_2(s\text{-trans-}\eta^2:\eta^2\text{-isoprene})$ (**31**) [57] and Mn(I), $[CpMn(CO)_2]_2((s\text{-trans-}\eta^2:\eta^2\text{-1,3-butadiene})$ (**32**) [58] having mode **F** (Fig. 1) have also been reported.



Recently a similar *s-trans*-1,3-butadiene coordination was found in a metal–metal bonded dinuclear iridium complex **34** having the A-frame structure (Fig. 5), which is an example of mode **D** in Fig. 1 [59]. At low temperature, the $[MeIr-Ir(CO)]^+$ moiety of **33** reversibly reacts with 1,3-butadiene to give a *s-trans*- $\eta^2:\eta^2$ -1,3-butadiene complex **34**, which transforms the diene ligand at 20 °C to give a bridging vinylvinylidene complex **35** through consecutive terminal hydrogen

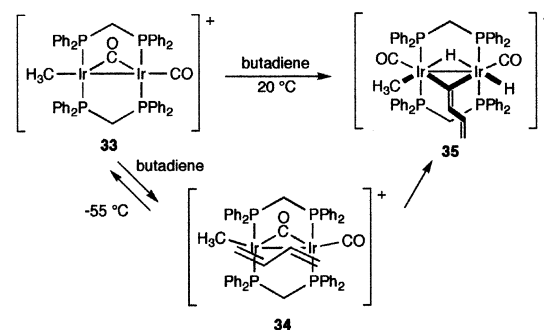
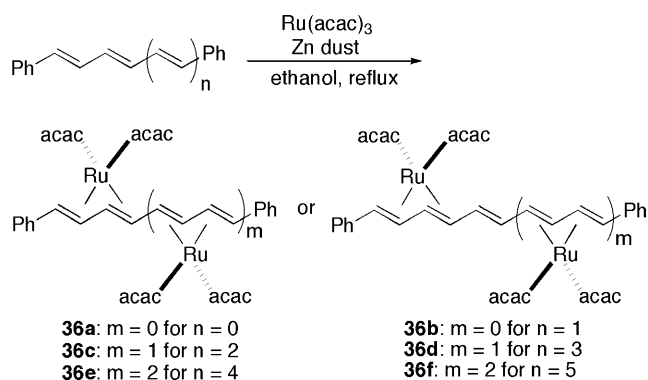
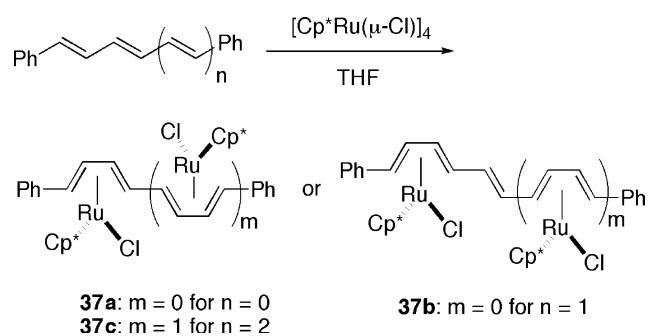


Fig. 5. The *s-trans* coordination of the bridging butadiene ligand to Ir_2 core [59].



Scheme 3.



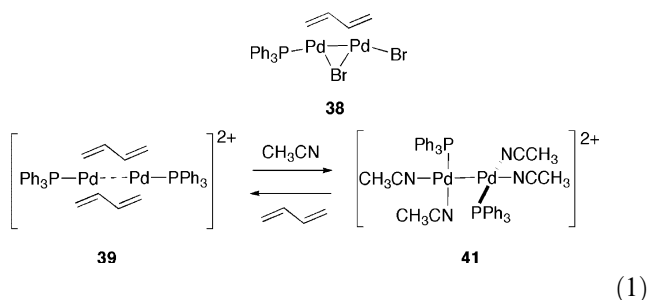
Scheme 4.

transfers to the metal. This is the first example of selective double activation for a *s-trans* butadiene ligand.

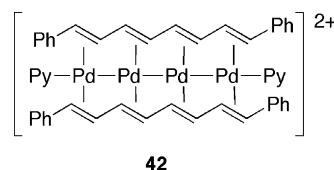
Extensively π -conjugated C=C bond systems (e.g. $\text{Ph}(\text{CH}=\text{CH})_n\text{Ph}$) were examined for the Ru complexation. A strong tendency for the *s-trans* coordination in the cases of ‘Ru(acac)₂’ fragments is observed for complexes **36** (Scheme 3), whereas the ‘RuCp*Cl’ fragments selectively coordinate in an *s-cis* fashion to the polyenes to give complexes **37** (Scheme 4) [60]. An electronic preference of the highly conjugated organic systems for the Ru fragment is thus apparent.

Recently, Kurosawa et al. have prepared a series of complexes containing *s-trans* diene coordinated to a Pd–Pd bond [61,62]. As evident from the experimental data, only *s-trans* isomers are found regardless of the substituents on the diene ligand. The di- σ bonding at the diene terminal carbon atoms is not allowed here since the metal prefers π -coordination from the filled diene orbitals. The preparative method is simple addition of the diene (substituted or unsubstituted) to an equimolar solution of a Pd(0) complex and a halopalladium(II) phosphine complex in dichloromethane. An asymmetrically coordinated complex $\text{Pd}_2(\mu\text{-Br})(\mu\text{-1,3-butadiene})(\text{PPh}_3)\text{Br}$ (**38**) could be prepared and structurally characterized by X-ray analysis [61]. It is of particular interest that a remarkably wide range of Pd–Pd bond lengths was observed among these diene complexes. A

bis(*s-trans*-1,3-butadiene) complex with two terminally coordinated triphenylphosphines $[\text{Pd}_2(\text{PPh}_3)_2(\text{s-trans-}\eta^2:\eta^2\text{-1,3-butadiene})_2]^{2+}$ (**39**) has a longer Pd–Pd bond of 3.185 Å, which is much longer than the Pd–Pd bond distance of **38** (2.662 Å), $\text{Pd}_2(\mu\text{-Cl})(\mu\text{-isoprene})\text{Cl}_2$ (**40**) (2.578 Å), and the dicationic complex $[\text{Pd}_2(\text{PPh}_3)_2(\text{CH}_3\text{CN})_4]^{2+}$ (**41**) (2.488 Å), which is derived from **39** and acetonitrile (Eq. (1)) [61,62]. The bonding nature of $\mu\text{-s-trans}$ -1,3-diene ligand was investigated by X-ray analysis and NMR measurements to reveal mostly σ -donation from each C=C double bond to the corresponding palladium atom. The C–C lengths are generally short–long–short just as in the cases of the mononuclear *s-trans*-1,3-diene ligand.



Furthermore, this simple synthetic method can be extended to a much longer conjugated π -system: 1,8-diphenyl-1,3,5,7-octatetraene coordinates in an all-*trans* fashion to a tetranuclear palladium array to form a unique sandwich chain complex **42** [63].



In summary, the *s-trans*-1,3-diene coordination mode has been found for various transition metal complexes, whose bonding character and some interesting reactivity are described. Moreover, this unique complexation mode has been observed in dinuclear and multinuclear cluster complexes, which might be future targets as organometallic materials.

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