



Diene complexes of early transition metals: ideas and progresses at Osaka University

Akira Nakamura^{a,*}, Kazushi Mashima^{b,*}

^a *OM Research, 7-2-1308, Minami-ohgimachi, Kita-ku, Osaka 530-0052, Japan*

^b *Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan*

Received 18 March 2004; accepted 3 August 2004

Available online 15 September 2004

Abstract

Historical perspectives for the chemistry of diene complexes of early transition metals developed at Osaka University in the period after 1970s were reviewed briefly and personally. Preparative chemistry of this field commenced from the magnesium–diene 1:1 compounds and quickly extended to almost all the early transition metals. By the studies operated together with other researchers, unique features of these diene complexes, especially their bonding and structure, selective reactions, and catalysis performances are described.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Diene; Early transition metal; Group 2 metals; Lanthanide metals; Polymerization

1. Introduction: Magnesium–diene adducts as the beginning

Organometallic chemistry has been filled with a full of unexpected discoveries and serendipitous findings. As we have enjoyed this particular field of chemistry for many years, we would like to summarize some of its unique aspects, especially the chemistry of 1,3-diene complexes of early transition metals. Of course, there have been many reviews and papers, which already covered this wide area of research so far [1–8], and thus we would like to focus ourselves to the parts which we feel much connected to our previous research in these 30 years at Osaka University.

In 1970–1976, assistant Prof. H. Yasuda co-operating with Prof. H. Tani had been working in the field of synthetic chemistry of organometallic compounds of main

group elements. He was then interested in the stereospecific polymerization of butadiene and isoprene with novel organometallic initiators such as organomagnesiums, RMgX , $\text{X} = \text{alkyl}$, etc. His group noticed a US Patent of Ramsden [9] and traced the reaction of butadiene and magnesium metal in various solvents. The hydrolysis of the organomagnesium products afforded very complex mixtures of oligomeric compounds and it was required much efforts to control these reactions. Nevertheless, Prof. K. Takase reported in 1970 that magnesium–diene reagents were useful for some purposes in natural product synthesis [10,11], and Prof. Otsuka and Dr. Akutagawa reported in 1976 that the magnesium compound of myrcene afforded some terpenoid compounds [12]. Under these severe competitions, Yasuda had made much efforts to find the best condition for preparing a pure crystalline magnesium–butadiene 1:1 adduct $\text{Mg}(\text{C}_4\text{H}_6)(\text{THF})_2$ (**1**) in good yields in 1976 [12]. This success was quickly extended to isoprene [13,14] and 2,3-dimethyl-1,3-butadiene [15] to obtain analogous 1,3-diene complexes, but not to 1,3-pentadiene or 2,4-hexadiene.

* Corresponding authors. Fax: +81 6 6850 6245.

E-mail addresses: YQB03164@nifty.ne.jp (A. Nakamura), mashima@chem.es.osaka-u.ac.jp (K. Mashima).

These magnesium compounds were weak in catalytic activity for oligomerization of these dienes at 40–60 °C without any selectivity [13]. The structure and reactivity were investigated utilizing conventional methods of organic chemistry as dianion sources (**A** in Chart 1) [10–12,16], but without any single-crystal X-ray diffraction study. Inability to obtain any crystalline complex suitable for the diffraction study remains even now to study the solid-state structure of these aliphatic diene–magnesium complexes. From 1977, we began cooperation with Yasuda and further extension into the transition metals was extensively surveyed. Afterwards, the problem of the solid-state structure of the diene–magnesium complexes was nicely solved by the X-ray analysis of 1,4-diphenyl-1,3-butadiene complex, $\text{Mg}(s\text{-cis-Ph-CH=CHCH=CHPh})(\text{thf})_3$ (**2**), in 1982 (see Fig. 1) [17]. Complex **2** was directly prepared by the reaction between magnesium metal and 1,4-diphenyl-1,3-butadiene. Furthermore, we found that the complex **2** was also prepared by the reaction of **1** and 1,4-diphenyl-1,3-butadiene (Eq. (1)) [18]. The presence of two terminal phenyl groups greatly helped to prepare the complex and to analyze the single-crystals in detail. Chelating *s-cis* structure was thus established and compared with the similar data of the Zr and Hf complexes prepared in the period 1978–1980. Prof. Raston et al. [19] reported magnesium–diene compound $\text{Mg}(\text{tmeda})(s\text{-cis-Me}_3\text{SiCH=CH-CH=CHSiMe}_3)$, which has much stronger σ -bonding character due to the presence of SiMe_3 groups at α -carbons.

Although the ligand exchange reaction described in Eq. (1) would be quite normal for transition metal diene complexes, it was curious that the organomagnesium compounds showed such the reactivity. We carried out exchange reactions of **2** with anthracene, cyclooctatetraene, and diphenylacetylene, giving the corresponding magnesium compounds **3–5** with the release of 1,3-butadiene [18]. We thus concluded, on the basis of these unique reactivities, that magnesium–diene compounds can be described by the canonical form **C**, not **A** nor **B** (Chart 1).

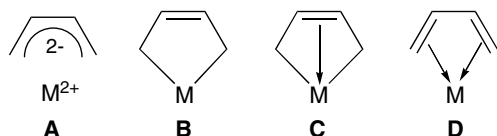
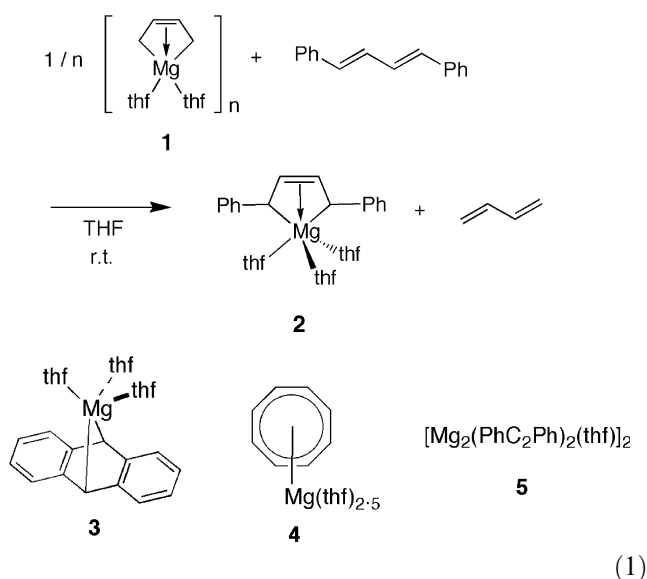
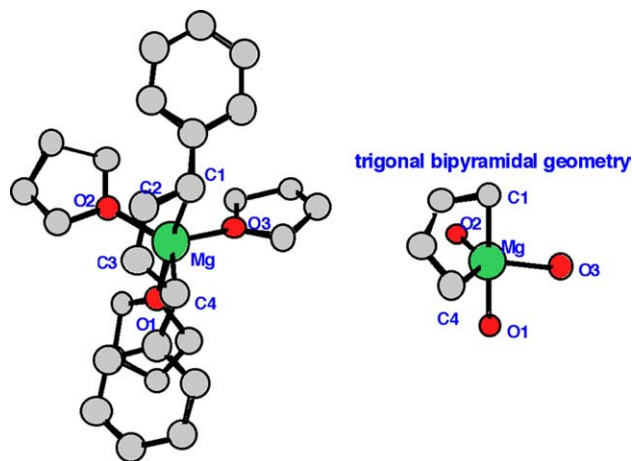
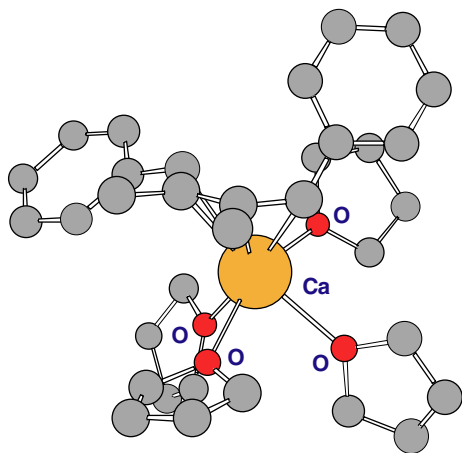
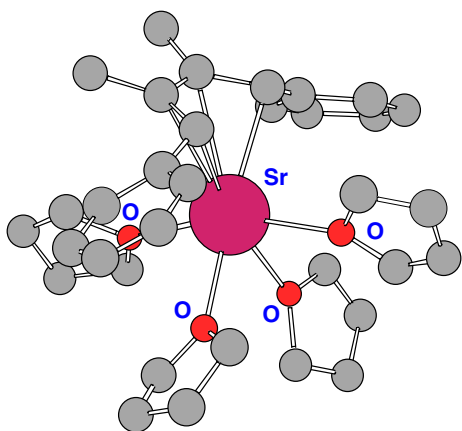


Chart 1.

Fig. 1. Crystal structure of 1,4-diphenyl-1,3-butadiene magnesium compound **2** [17].

These results prompted us to anticipate that heavier group 2 elements such as calcium and strontium may have a larger contribution of form **C** as a canonical form and show unique structural feature and reactivity. The best synthetic idea we examined was the reaction of group 2 metals with 1,4-diphenyl-1,3-butadiene. The metals were consumed on heating to give diene adducts as air sensitive insoluble solids, whose characterization was hampered by their poor solubility. On introducing two methyl groups at 2,3-positions of 1,4-diphenyl-1,3-butadiene, we were able to prepare the diene complexes of magnesium, calcium, and strontium, $\text{M}(\text{mpbd})(\text{thf})_4$ (**6**: $\text{M} = \text{Mg}$; **7**: $\text{M} = \text{Ca}$; **8**: Sr ; $\text{MPBD} = 2,3\text{-dimethyl-1,4-diphenyl-1,3-butadiene}$) [20]. The X-ray structures of **7** and **8** are shown in Figs. 2 and 3, respectively. In complex **8**, the ipso carbon of one of two phenyl groups interacted with the strontium center. The diene bonding of the calcium and the strontium complexes in solution, as judged from the sp^n hybridization at the terminal $J_{\text{C-H}}$ values, indicated an interesting trend having the form **C** with a contribution of the canonical form **D**, as shown in Fig. 4. The strontium complex has the largest value of $\text{sp}^{2.5}$ among three complexes, being comparable to that of

Fig. 2. Crystal structure of **7** [20].Fig. 3. Crystal structure of **8** [20].

zirconocene butadiene complex, while the magnesium complex has strong Mg–C σ -bonds. This difference is attributed to an increase of the coordination sphere of heavier group 2 elements.

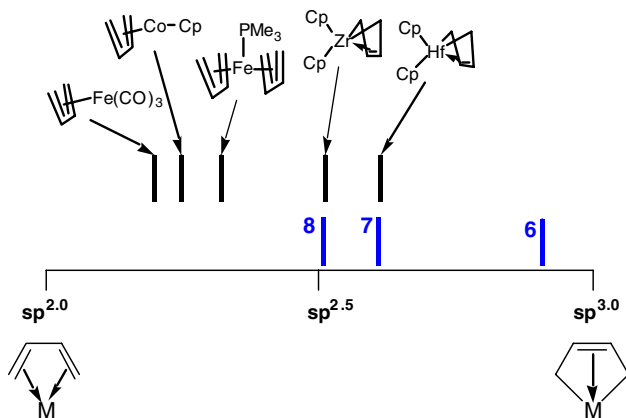


Fig. 4. Nature of the bond between metal and terminal carbons in the diene complexes of group 2 elements and some transition metals as estimated by ^{13}C NMR spectroscopy.

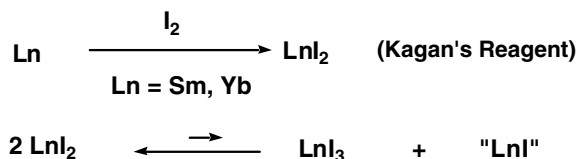


Fig. 5. Proposed disproportionation of Kagan's reagent, SmI_2 .

2. Lanthanoids and actinoids diene complexes

When we were interested in diene complexes of lanthanoids and actinoids elements, there were a limited number of examples: metallocene derivatives such as $\text{Cp}_2^*\text{Th}(1,3\text{-butadiene})$ [21,22], $\text{Cp}_2^*\text{U}(1,3\text{-butadiene})$ [23], and $\text{LaCp}_2^*(\text{thf})\{\mu-(\eta^1:\eta^3\text{-butadiene})\text{LaCp}_2^*\}$ [24] were reported. On the other hand, two equivalents of Kagan's reagent, SmI_2 , were reported to be required to reduce a wide variety of organic substrates [25]. We proposed that two equivalents of SmI_2 were in equilibrium with a mixture of SmI_3 and 'SmI' species (Fig. 5), the latter of which acts like magnesium metal. This idea led to successful preparation of cyclooctatetraenyl complexes with the general formula, $(\eta^8\text{-C}_8\text{H}_8)\text{LnI}(\text{solvent})_n$ (**9**) [26].

We started a project to prepare diene complexes of lanthanoid elements. After some efforts, we found that the reaction of metallic lanthanum with one equiv. of iodine and half equiv. of 1,4-diphenyl-1,3-butadiene in THF at 50 °C for 48 h afforded an inverse sandwich type complex $\text{LaI}_2(\text{thf})_3\mu-(\eta^4:\eta^4\text{-1,4-diphenyl-1,3-butadiene})\text{LaI}_2(\text{thf})_3$ (**10**) as red crystals [27]. Structure of **10** was characterized by X-ray analysis (Fig. 6). It is of interest that the geometry of complex **10** is similar to that of the dilithium compound of 1,4-diphenyl-1,3-butadiene, $\text{Li}(\text{tmeda})\{\mu-(1,4\text{-diphenyl-1,3-butadiene})\}\text{Li}(\text{tmeda})$ (**11**) [28], which has the same diene-bridged structure as **10**. Thus, LaI_2 moieties in the complex **10** acts as the lithium metals in **11**.

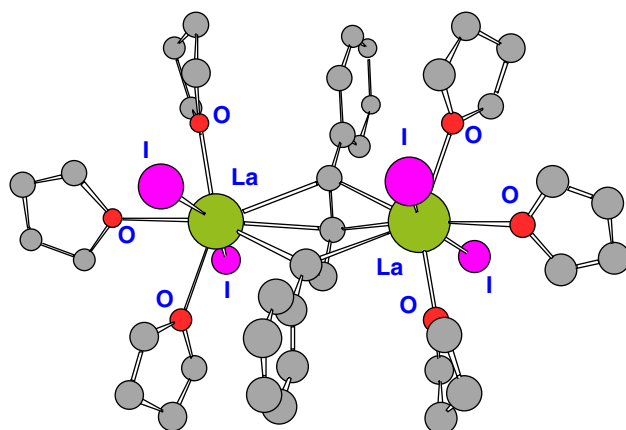
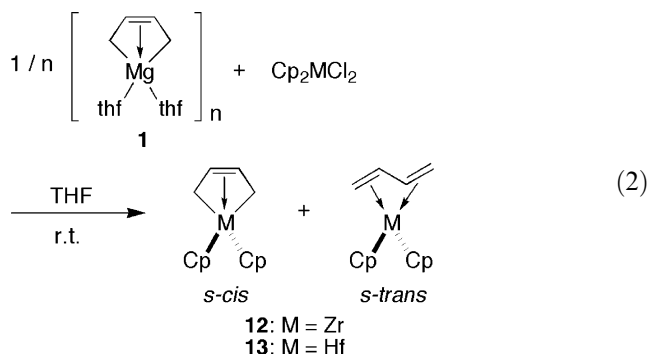


Fig. 6. Crystal structure of **10** [27].

3. Zirconocene diene complexes

Importance of the magnesium–diene 1:1 adducts for the general preparation of 1,3-diene complexes of a variety of transition metal complexes was soon revealed. The first successful application was achieved for the preparation of zirconocene diene complexes in 1978 at Osaka University. The first trials of reaction of zirconocene dichloride and hafnocene dichloride with the magnesium reagents in a 1:1 molar ratio in THF were conducted by a graduate student Mr. Y. Kajiwara, giving the corresponding diene complexes in good yields (Eq. (2)). These have high reactivity to various unsaturated organics. In particular, the catalysis of these zirconium compounds for oligomerization of butadiene or isoprene was found at 60 °C to give linear dimers stereoselectively. The first report was made in 1979 at the 9th ICOMC (Dijon) and attracted a considerable interest [29]. While our communication to JACS was rejected, an important paper of Prof. G. Erker (Univ. Bochum) appeared in JACS in 1980 [30]. It was quite an unexpected occasion that the same *s-cis*-diene complexes of zirconocene were prepared concurrently by Erker's group, who used photolysis of diphenyl zirconocene in the presence of dienes. Soon after our report [15,29,31], Erker had started to use our synthetic method by using magnesium–butadiene for the preparation of the butadiene complexes of zirconocene, Cp₂Zr(η⁴-1,3-butadiene) (**12**), and hafnocene, Cp₂Hf(η⁴-1,3-butadiene) (**13**) [32], and Dr. S. Wreford (du Pont) had also applied the magnesium–butadiene compound for the synthesis of some diene complexes of group 4–8 metals [33].



To our great surprise, the Erker's group showed a remarkable *s-trans* coordination of the diene to Zr by the X-ray evidence [30]. This was the first paper on *s-trans*-diene coordination to the mononuclear metal center, and thus the unique properties of zirconium in such extended coordinative interaction attracted interest of many organometallic chemists. Since the *s-trans* coordination produced molecular chirality, disorder of isomers, (*R*) and (*S*), at the diene caused positional ambiguity of the carbons and hydrogens of the ligand. Therefore, remarkably large error limits were reported

in the X-ray parameters for the *s-trans* complex **12** [30]. We felt crucial needs for more precise X-ray results for the unique new type of coordination mode.

Thus, more rigid and sterically demanding substituents are sought and, finally, 1,4-diphenylbutadiene was selected for that purpose. The preparation of the required magnesium complex **2** led to a successful result that the zirconocene complex, Cp₂Zr(*s-trans*-PhCH=CHCH=CHPh) (**14**) was similarly made [15]. Alternatively, complex **14** was prepared by the ligand exchange reaction of the butadiene zirconocene complex **12** with free 1,4-diphenyl-1,3-butadiene. Fortunately, this complex **14** was found to be mostly *s-trans* coordinated by the NMR data and the single-crystals were examined by X-ray with the help of Prof. N. Kasai and Dr. Y. Kai (Osaka University). Our collaborative study clarified the precise parameters of the *s-trans*-diene ligand for the first time in early 1982 (see Fig. 7) [34].

It was a really good collaboration with Dr. K. Tatsumi who just came back to Japan from the Hoffmann's group at Cornell University and joined our group in 1981. He made an important contribution to the chemistry of the diene complexes from the theoretical viewpoints. He analyzed the bonding nature of diene and the zirconocene fragments by using the EHMO method, and clearly showed that the *s-trans* coordination should be preferred by terminal substituent(s) such as methyl and phenyl [35].

Having all the ¹H NMR parameters of *s-cis* and *s-trans* isomers of zirconocene diene complexes, we looked at the NMR spectra just after our preparation. We found that our method also produced the *s-trans* isomer (Eq. (2)). At that time, we thought that signals due to the *s-trans* isomer were ascribed to impurities because our method of purification was conventional recrystallization, in which a short heating of a solution actually converted it to the *s-cis* isomer by thermal isomerization. By this time, Erker's group completed the energetics of the *s-trans* vs. *s-cis* isomerization and concluded that the *s-cis* isomer is more stable [30].

Based on the theoretical prediction by Tatsumi that the total energy of the *s-trans*-(2,4-hexadiene)zirconium complex is slightly lower than that of the *s-cis* isomer, we had tried to prepare some alkyl-substituted diene

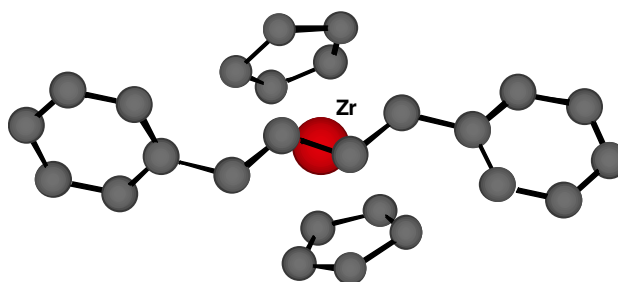
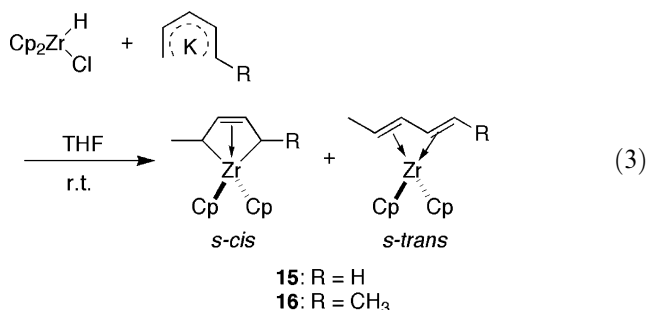
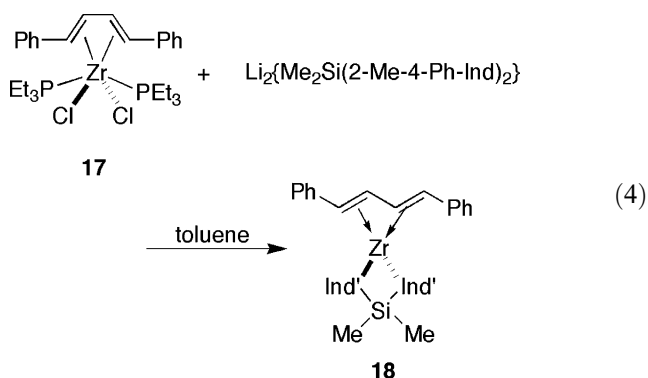


Fig. 7. Structure of the *s-trans*-diene complex of zirconocene **14** [34].

complexes of zirconium. Fortunately, we utilized Yasuda's previous results on alkyl-substituted pentadienyl potassium for the preparation of such diene complexes [36,37]. Thus, the reaction of some of the alkylated pentadienyl potassium with zirconocene hydrochloride was found to give mono- or bis-alkylated diene complexes in good yields [38]. Actually, (*E*)-1,3-pentadiene complex **15** and (*E,E*)-2,4-hexadiene complex **16** were found to be a mixture of *s-cis* and *s-trans* isomers (Eq. (3)). The prediction of Tatsumi was correct. The preparative success provided a series of zirconocene complexes of alkyl-substituted dienes to be readily prepared by this route.



It is noteworthy that, quite recently, a new diene complex of divalent zirconium **17** has been applied for the stereoselective synthesis of the *C*₂ ansa-type *s-trans*-diene zirconium complex **18**, which catalyzes the iso-specific polymerization of propylene with MAO (Eq. (4)) [39].



Recently, Erker reported that a cationic diene complex of tantalocene [*Cp*₂Ta(*s-trans*- η^4 -butadiene)]⁺ (**19**), which is isoelectronic and isolobal to that of hafnocene and exhibits similar structural feature and reactivity [40–43].

4. Monocyclopentadienyl derivatives

As mentioned above, the utility and usefulness of the magnesium–diene compounds as convenient reagents to prepare a wide variety of diene complexes of many other transition metals, especially early transition metals, was beginning to be well recognized. Aiming at extension to

the neighboring metals, we started the synthesis of diene complexes of niobium and tantalum in early 1982. The chemistry of these metals had just started to draw an attention of organometallic chemists, since alkylidene and alkylidyne complexes of these metals were found by Prof. R. Schrock [44,45]. We had chosen half-metallocene compounds (η^5 -C₅R₅)MCl₄ (M = Nb and Ta) as the most convenient source for our purpose because they have convenient solubility and easily give alkyl species such as Cp*TaMe₄. At that time, only a few of organotin reagents (e.g., *n*-Bu₃SnCp) have been known for the preparation from the metal pentachloride [46,47]. The preparative reaction with metal chlorides resulted in the formation of trialkyltin chloride, a toxic and nasty waste. We have examined a silicon analog of these reagents and found it to be more convenient and of wide applicability [48]. Especially, in the large scale, removal of the by-product, e.g., Me₃SiCl, is quite easy and thus the monocyclopentadienyl products are of high purity in general. Similarly, Cp* derivatives of these metals can also be made. After these successful results, we also extended this silicon method to prepare half-metallocene complexes of titanium (see Fig. 8).

It was not difficult for us to isolate a variety of air-sensitive half-metallocene diene complexes. Before our synthesis, only a few examples were known for the half-metallocene diene complexes of the type CpM(diene)X. For example, the one with tantalum, Cp*Ta(*s-cis* η^4 -1,3-butadiene)[(CH₂)₄], was prepared by the reaction of Cp*Ta(PMe₃)₂H₄ with ethylene [49]. The observed dehydrodimerization of ethylene was of particular interest in relation to a catalytic counterpart of this reaction reported by G. Pez in 1977, which a binuclear CpTi species catalyzed conversion of ethylene to ethane and butadiene and he postulated a butadiene bridging binuclear complex [50].

In 1983, Erker's group [51,52] and Teuben's group [53–57] had started to prepare group 4 metal complexes.

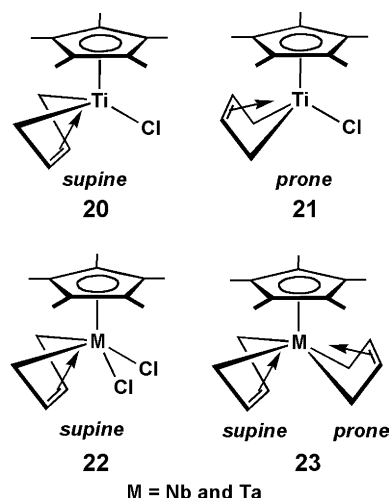


Fig. 8. Half-metallocene diene complexes and the nomenclature.

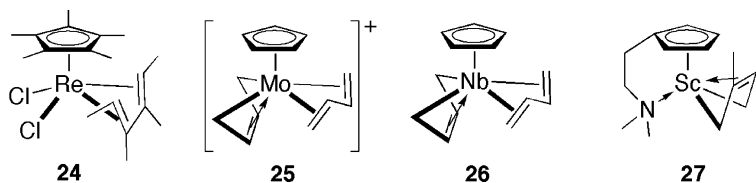


Fig. 9. Some examples of half-metallocene diene complexes.

A series of diene complexes of Ti [58,59], Nb [60] and Ta [61,62] is shown in Fig. 8. Prof. Herberich [63,64] and Prof. Ernst [65] also reported similar diene complexes of niobium. The presence of one Cp ligand gives rise to the geometrical isomerism, which is classified by terms ‘supine’ and ‘prone’ according to the proposal of Yasuda in 1984. This indication is felt important and conveniently used to indicate the complexes of this kind later by many organometallic chemists worldwide [4].

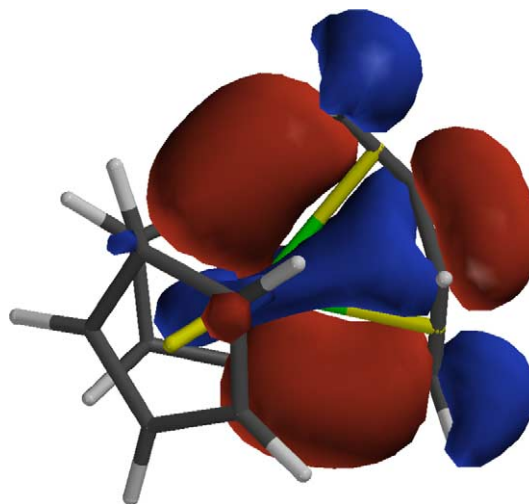
The observed *supine*–*prone* orientation of the bis(diene) complexes is unique for the early transition metals as contrasted by the *supine*–*supine* ones already known for bis(diene) complexes of Mn(0) and Rh(I). Very recently, some other bis(diene) complexes of molybdenum [66–68] and tungsten [69] were found to have the same *supine*–*prone* geometry.

Once the chemistry of this type of complexes started, several other interesting complexes have been prepared. A rhenium diene complex **24** and a cationic molybdenum complex **25** were respectively prepared by Prof. W. A. Herrmann in 1989 [70] and Prof. R. Poli in 1997 [66–68]. The molybdenum complex is isoelectronic and isostructural with the parent niobium one **26**. The scandium complex **27** was recently prepared by Prof. B. Hessen and Prof. J. Teuben [71] (see Fig. 9).

5. Nature of metal–diene bonding

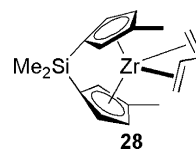
Since the d-orbitals for the early transition metals are much higher in energy compared with those of the late transition metals, an extensive back donation from the diene ligands to the early transition metals occurs in *s-cis* as well as *s-trans*-diene complexes. The X-ray structural parameters of these diene complexes clearly indicate the importance of such orbital interactions, especially for the *s-cis* isomer. The terminal C–C bonds of the *s-cis* diene part are elongated, while the central C–C bond is shortened, resulting in the long-short-long sequence of the C–C bonding and the σ – π – σ extreme for the diene-metal bonds as shown in Chart 1, C.

The coordinative interaction of the *s-trans*-diene complexes is quite different from that of the *s-cis* ones. Here, the back donation from the metal to the *s-trans*-diene moiety is attributed to the somewhat extended d-orbital (a_2 symmetry), as shown in Fig. 10, which was revealed by a recent density functional MO calculations

Fig. 10. Back donative interaction in *s-trans*-butadiene zirconocene **12** [72].

(BP 86) [72]. This unique interaction makes the three Fig. 10 C–C bonds in the *s-trans*-diene moiety almost equidistant from each other. The two terminal carbons are pulled inwards to the metal through the back donation, leading to the short metal–(terminal carbon) distances (see Table 1). The distortion of the diene by the coordination to early transition metals thus occurs in *s-cis* in the ligand plane, but in *s-trans*, out of the plane.

After the first precise X-ray data for **14**, it was quite difficult to obtain further data for some other *s-trans*-diene complexes because of the inherent disorder at the diene ligand. Only recently, such data for the *ansa*-zirconocene diene complexes **18** [39] and **28** [73] have been reported [34]. These unique features are listed in Table 1.



The electronic effect of the unique *s-trans*-diene ligand has been revealed as accumulating the spectral data, indicating that the *s-trans* diene ligand has more electron-donating feature relative to the *s-cis* ones as evident from the NMR data of relevant diene complexes of *s-cis* and

Table 1
Comparison of the relevant bond distances (Å) in the mononuclear *s-trans*-diene complexes

| Compound | M–C(terminal) | M–C(central) | C(terminal)–C(central) | C(central)–C(central) | Ref. |
|----------|---------------|--------------|------------------------|-----------------------|------|
| 14 | 2.509 | 2.391 | 1.435 | 1.467 | [34] |
| | 2.503 | 2.399 | 1.403 | | |
| 18 | 2.523(2) | 2.394(2) | 1.423(3) | 1.412(2) | [39] |
| | 2.515(2) | 2.387(2) | 1.417(3) | | |
| 28 | 2.453(3) | 2.352(3) | 1.402(5) | 1.393(5) | [73] |
| | 2.455(3) | 2.338(3) | 1.364(6) | | |

s-trans structure. These differences are already discussed more fully in our paper in 2002 [5]. Interesting thermochromism of the *s-trans*-1,4-diphenylbutadiene complex of zirconocene was detected in the solid state and correlated to the rotation of the two phenyl rings of the ligand as a result of the collaboration with Prof. S. Takeda, who confirmed significant shifts of the chemical shift values on the temperature variation by using solid-state proton NMR measurement of the complex [74].

6. Functionalized diene complexes

We have reported the stereoselective addition of organic carbonyl and some other unsaturated compounds to the zirconocene diene complexes (vide infra). In the case of the diene complexes of niobium and tantalum, the diene ligand was found to be much stronger bound to the metal and therefore such addition reactions are sluggish [62]. Thus, we realized that the diene ligand bound to the group 5 metals works as a spectator ligand for some organometallic catalyses, and that the monodiene complexes with two halo ligands, Cp(diene)MX₂, are isoelectronic to the metallocene dihalides of the corresponding group 4 metals. This idea prompted us to prepare dialkyl derivatives as shown in Fig. 11.

These complexes are 16-electronic complexes just like the well-known zirconocene dialkyls. It was well demon-

strated that a cationic 14-electron alkyl complex of zirconocene is a key species to polymerize 1-alkenes. Thus, we thought that the corresponding 14-electronic cationic alkyl complexes of tantalum are generated by reaction of the dimethyl tantalum complex **30** with excess MAO [75–77]. The first trial of this reaction was evidenced by a smooth color change from purple to yellow just upon the mixing. Polymerization of ethylene by using the tantalum catalyst systems was really very slow. Three different diene ligands with each of the isostructural niobium and tantalum analogues were examined to find the dimethylbutadiene/Nb combination was the best for the polymerization, and the polymerization by using this system at low temperature afforded a unique polyethylene with extremely narrow polydispersity, whose value reached to 1.05 with *M_w* of 20,000. Examination of this polymer with GPC gave an unusually sharp peak, indicating a living polymerization. R. Poli recently reported that diene half-metallocene molybdenum complexes became catalyst precursors for ethylene polymerization [78]. The mechanism of these catalyst systems was discussed on the basis of DFT calculations [78,79].

A plausible intermediate, cationic 14-e species [Cp(diene)MR]⁺ (M = Nb and Ta), seemed quite unstable without any 2-e donor ligand and would readily coordinate ethylene giving a 16-e species which initiates the polymerization. The thermal instability of the 14-e species is the cause of the lower polymerization activity above 30 °C. A delicate balance between the insertion

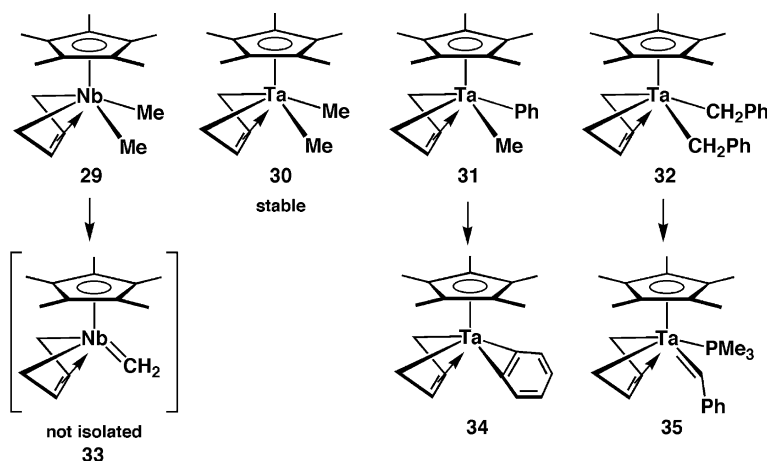


Fig. 11. Some derivatives of half-metallocene complexes of tantalum.

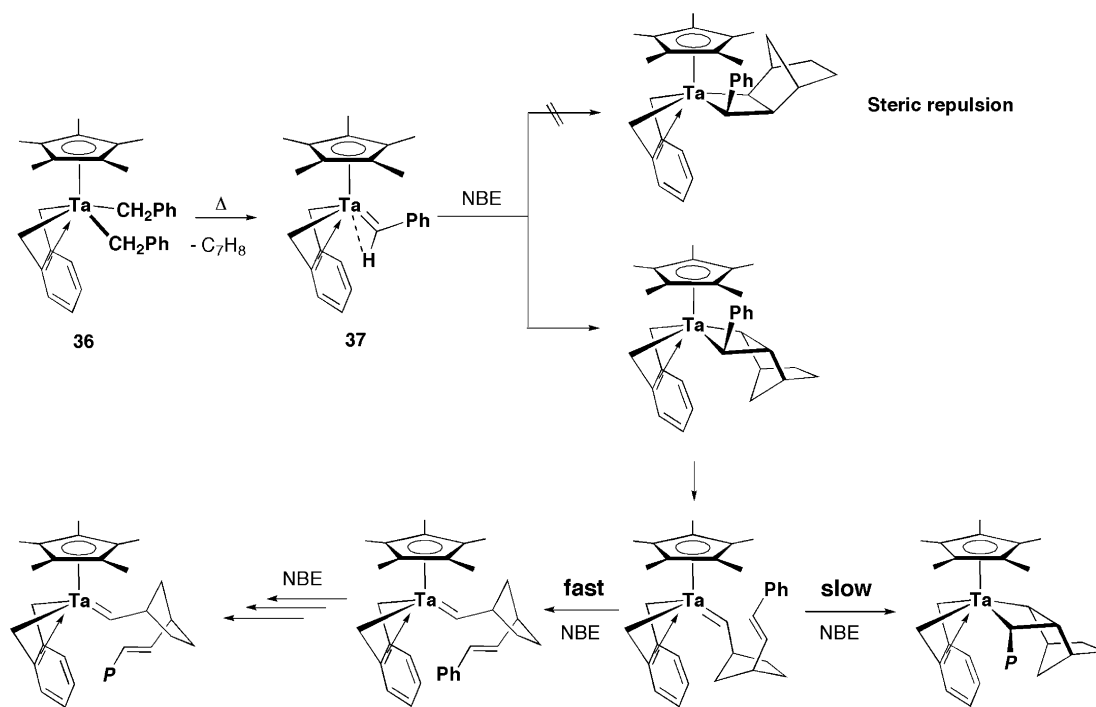
rate of ethylene and life times of the cationic initiator determines the polymer molecular weight observed. The diethyl analog, $\text{Cp}^*(\text{butadiene})\text{TaEt}_2$, was found to give an ethylene complex that can be isolated by addition of PMe_3 [80].

Generally, these dialkyls or diaryls are decomposed by elimination of alkanes or arenes respectively to give reactive carbene [81–83] or benzyne [84] complexes with 16-electron count. We found that the dimethyl complex of niobium, $\text{Cp}^*\text{NbMe}_2(\eta^4\text{-butadiene})$ (**29**), decomposed at 60 °C to give a reactive methylene species, which was trapped by addition of an ester and norbornene respectively to give a vinyl ether and a metallacyclobutane derivative [82], while the dimethyl complex of tantalum, $\text{Cp}^*\text{TaMe}_2(\eta^4\text{-butadiene})$ (**30**), was found to be thermally more stable. It is noteworthy that this difference of reactivity is corresponding to the difference between titanocene dimethyl and zirconocene dimethyl complexes. In contrast, di(benzyl) complexes of tantalum, $(\eta^5\text{-C}_5\text{R}_5)\text{Ta}(\text{CH}_2\text{Ph})_2(\eta^4\text{-butadiene})$ (**32**), underwent α -hydrogen abstraction and elimination of toluene, affording a benzyldiene complex, $(\eta^5\text{-C}_5\text{R}_5)\text{Ta}(\text{=CH-Ph})(\eta^4\text{-butadiene})(\text{PMe}_3)$ (**35**), which catalyzed rapid ROMP of norbornene to give poly(norbornene)s in the absence of PMe_3 . *cis-trans* selectivity at the polymer chains was absent with the ‘ $\text{CpTa}(\eta^4\text{-butadiene})$ ’ catalysis, but considerable *cis*-selectivity (98%) was observed with the ‘ $\text{Cp}^*\text{Ta}(\eta^4\text{-butadiene})$ ’ catalysis [81,83]. The structure of the diene ligand was found to

influence the selectivity, and thus the tantalum complex **36** with the xylylene ligand instead of the butadiene ligand and promoted the formation of all-*trans* (about 93%) polymers [83]. The stereochemical route for all-*trans* polymers is shown in Fig. 12.

These observations can be attributed to different conformation of the metal-carbene intermediates, an *anti*-rotamer for the xylylene catalyst and a *syn*-rotamer for the xylylene catalyst. The DFT optimization of various benzyldiene species was performed for the corresponding niobium analogs with the xylylene ligand [72]. The preferred formation of benzyldiene species of the perpendicular geometry leading to the formation of the *trans*-polymer was suggested. The orientation of the phenyl on the benzyldiene ligand is stabilized by the specific α -agostic interaction (narrow Nb–C–H angle, 87°) with the niobium center. The Nb–C–C(Ph) angle is thus considerably widened and the steric crowding between Cp^* ligand and the Ph part of the benzyldiene ligand is eliminated.

This result indicates that the identity of diene ligand is important for controlling the stereoselective reaction of the carbene moiety. Since the diene ligands are distorted by the coordination to the metal, its influences should be considered by detailed analysis of the mutual inter-ligand interactions in the reaction intermediates. This is a unique three-dimensional electron conjugation taking place in the diene-carbene complexes, and is different from simple picture as predicted from the chemical formula. Recently, some outcome of the



P = *Trans*-poly(norbornene)

Fig. 12. Selective formation of all-*trans* polymers by the catalysis of $\text{Cp}^*(\eta^4\text{-xylylene})\text{Ta}(\text{=CHPh})$ complex (**36**) [83].

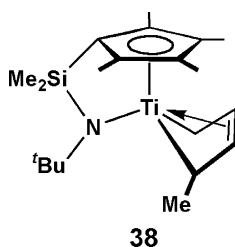
inter-ligand interaction was clearly shown in the thermal reaction of diene–carbene iron carbonyl complexes [85].

7. Reactions and catalysis

Although some of the regioselective reactions of zirconocene diene complexes have been described fragmentally, prominent advantages in organic synthesis are briefly described here [86–90]. The most striking regio-selection was found in the addition reaction of carbonyl or olefinic bond to the isoprene complex, $\text{Cp}_2\text{Zr}(\eta^4\text{-isoprene})$ [86–88]. The selectivity reached to 98% in the cases of addition of somewhat bulky ketones [86]. The selective formation of new metallacycles is realized upon addition of various α -olefines [87]. Tandem insertion reactions afforded 9-membered metallacycles [89,90]. These results were obtained in competition with Erker's group, who reported essentially the same insertion reactions with the butadiene complex of zirconocene [91–94]. Furthermore, we carried out the reactions of diene complexes of group 5 metals and found that essentially the same carbonyl additions proceeded in the cases of the bis(diene) complexes of niobium and tantalum [60,62].

The coordination ability of *s-trans* coordination mode is weaker than that of *s-cis* one. Unusual diene–alkene exchange reaction of some particular *s-trans*-diene complexes was observed. Thus, *s-trans*-2,4-hexadiene complex readily undergoes such exchange reaction to give a zirconacyclopentane complex, which was converted to cyclopentanones on reaction with CO followed by the protolysis [95].

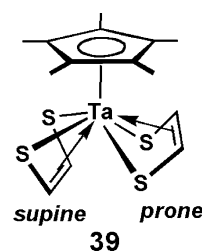
Such a lability of the diene ligand was applied to generate catalytically active species. In 1993, we found that the 14-e cationic alkyl species catalytically active for the ethylene polymerization were readily generated by the diene transfer reaction of bis(diene) complexes **23** of niobium and tantalum with alkyl aluminums, e.g., MAO [76,77]. This result suggested a new idea that diene complexes of zirconocene could be activated by MAO or $\text{B}(\text{C}_6\text{F}_5)_3$. Our experiment afforded a result that catalytic performance of the diene complexes was better than the corresponding dichloride or dimethyl precursors. In 1995, our approach has been followed by G. Erker for treating the butadiene zirconocene **12** with $\text{B}(\text{C}_6\text{F}_5)_3$



[7,8,96] and by Prof. T.J. Marks for the diene CGC complexes **38** of titanium with $\text{B}(\text{C}_6\text{F}_5)_3$ or MAO [97].

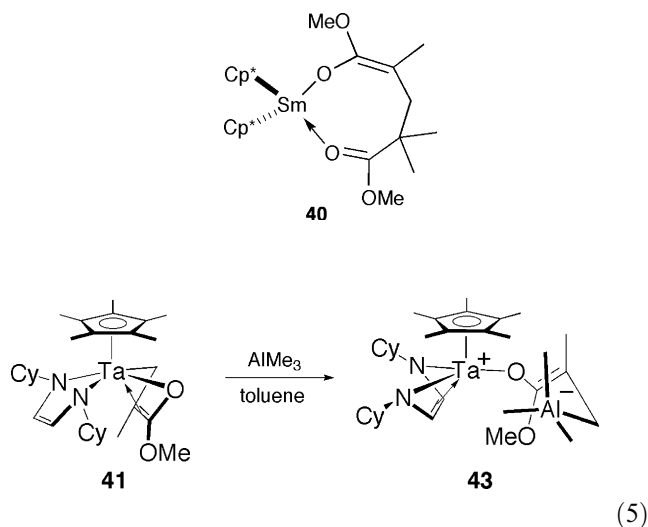
8. Heterodiene complexes

Since the publication of the 1-azadiene complex of iron carbonyl [98], we have been interested in the heterodiene ligands such as 1,4-dithia-1,3-butadiene, 1-aza-1,3-butadiene, 1,4-diaza-1,3-butadiene, and dithia-1,3-butadiene because these ligands showed unique coordination modes [5]. Our approach has been based on the coordination space of half-metallocene fragments of niobium and tantalum, in which various catalytic and stoichiometric transformations have been performed. Tatsumi prepared bis(1,4-dithia-1,3-butadiene) complex, $\text{Cp}^*\text{Ta}(\text{SCH}=\text{CHS})_2$ (**39**), that adopts *supine-prone* orientation [99]. The unique C–S bond fission of **39** led to the chemistry of the sulfide complexes such as $[\text{Cp}^*\text{Ta}(\text{S})_3]^{2-}$ (**40**) [100], and since then he has been extending this line of the chemistry.



Azadiene [101–103] and diazadiene [104,105] complexes of niobium and tantalum also showed unique *supine* and *prone* orientations depending on substituent(s) on not only ligands and also on metal center. In case of azadiene complexes, we found some interesting C–C bond formation reactions of the ligand [106]. Prof. J. Scholz concurrently reported some interesting aza- and diazadiene complexes of early transition metals and their unique transformations [107–116].

We have been interested in oxa-diene complexes because a samarocene initiator, Cp^*SmH , polymerized MMA in a living manner to give monodispersed syndio-specific PMMA through the samarium-enolate intermediate, **40** [117–119]. Recently, 1-oxa-1,3-diene complexes of tantalum, $\text{Cp}^*\text{Ta}(\eta^2\text{-Cy-DAD})(\eta^4\text{-MMA})$ (**41**) and $\text{Cp}^*\text{Ta}(\eta^4\text{-1,3-butadiene})(\eta^4\text{-MMA})$ (**42**) (Cy-DAD = 1,4-Dicyclohexyl-1,4-diaza-1,3-butadiene) were prepared, and they became catalyst precursors for MMA polymerization [120]. Activation of the MMA moiety bound to the tantalum center by 1 equiv of AlMe_3 afforded a zwitterionic enolate species **43** (Eq. (5)), which catalyzed the polymerization of MMA in living manner to give PMMA with *syndio*-selectivity (rr up to 71%) and narrow polydispersity ($M_w/M_n = 1.11$) below -20°C .



9. Further prospects

A new stream of early transition metal organometallic chemistry began by introduction of the magnesium–diene compounds as reagents and a rich new field of research was created. This field already encompasses from theoretical aspect to applicable one, and the scope is expected to be wider in future. Conceptual advance has been frequently achieved upon the development of each facet of the diene complex chemistry. A new concept of “Organometallic Conjugation” is thus created to summarize the whole field and a book edited by one of the authors appeared in 2002 [121].

Most of the fundamental information required for further progress has now been secured and we can see bright future of this field of organometallic chemistry.

Acknowledgements

We appreciate Professor H. Yasuda (Hiroshima University), Professor K. Tatsumi (Nagoya University), and co-workers whose name appeared in literatures.

References

- [1] H. Yasuda, K. Tatsumi, A. Nakamura, *Acc. Chem. Res.* 18 (1985) 120.
- [2] H. Yasuda, A. Nakamura, *Angew. Chem., Int. Ed. Engl.* 26 (1987) 723.
- [3] A. Nakamura, K. Mashima, *J. Organomet. Chem.* 500 (1995) 261.
- [4] A. Nakamura, K. Mashima, *J. Organometal. Chem.* 621 (2001) 224.
- [5] K. Mashima, A. Nakamura, *J. Organomet. Chem.* 663 (2002) 5.
- [6] G. Erker, C. Krueger, G. Mueller, *Adv. Organometal. Chem.* 24 (1985) 1.
- [7] G. Erker, *Acc. Chem. Res.* 34 (2001) 309.
- [8] G. Erker, *Chem. Commun.* (2003) 1469.
- [9] H.E. Ramsden, US Patent no. 1968, 3388179; *Chem. Abst.* 69, 67563d, 1968.
- [10] M. Yang, K. Yamamoto, N. Otake, M. Ando, K. Takase, *Tetrahedron Lett.* (1970) 3843.
- [11] M. Yang, M. Ando, K. Takase, *Tetrahedron Lett.* (1971) 3529.
- [12] S. Akutagawa, S. Otsuka, *J. Am. Chem. Soc.* 98 (1976) 7420.
- [13] H. Yasuda, Y. Nakano, K. Natsukawa, H. Tani, *Macromolecules* 11 (1978) 586.
- [14] Y. Nakano, K. Natsukawa, H. Yasuda, H. Tani, *Tetrahedron Lett.* (1972) 2833.
- [15] H. Yasuda, Y. Kajiwara, K. Mashima, K. Nagasuna, K. Lee, A. Nakamura, *Organometallics* 1 (1982) 388.
- [16] (a) R.D. Rieke, *Science* 246 (1989) 1260;
(b) H. Xiong, R.D. Rieke, *J. Org. Chem.* 54 (1989) 3247;
(c) R.D. Rieke, H. Xiong, *J. Org. Chem.* 56 (1991) 3109;
(d) H. Xiong, R.D. Rieke, *Tetrahedron Lett.* 32 (1991) 5269;
(e) H. Xiong, R.D. Rieke, *J. Am. Chem. Soc.* 114 (1992) 4415;
(f) M.S. Sell, H. Xiong, R.D. Rieke, *Tetrahedron Lett.* 34 (1993) 6011;
(g) M.S. Sell, H. Xiong, R.D. Rieke, *Tetrahedron Lett.* 34 (1993) 6006.
- [17] Y. Kai, N. Kanehisa, K. Miki, N. Kasai, K. Mashima, H. Yasuda, A. Nakamura, *Chem. Lett.* (1982) 1277.
- [18] K. Mashima, Y. Matsuo, H. Fukumoto, K. Tani, H. Yasuda, A. Nakamura, *J. Organometal. Chem.* 545/546 (1997) 549.
- [19] M.G. Gardiner, C.L. Raston, F.G.N. Cloke, P.B. Hitchcock, *Organometallics* 14 (1995) 1339.
- [20] K. Mashima, H. Sugiyama, K. Kanehisa, Y. Kai, H. Yasuda, A. Nakamura, *J. Am. Chem. Soc.* 116 (1994) 6977.
- [21] G. Erker, T. Mühlenbernd, R. Benn, A. Rufinska, *Organometallics* 5 (1986) 402.
- [22] G. Erker, T. Mühlenbernd, A. Rufinska, *Chem. Ber.* 120 (1987) 507.
- [23] G.M. Smith, H. Suzuki, D.C. Sonnenberger, V.W. Day, T.J. Marks, *Organometallics* 5 (1986) 549.
- [24] A. Scholz, A. Smola, J. Scholz, J. Löbel, H. Schumann, K.-H. Thiele, *Angew. Chem., Int. Ed. Engl.* 30 (1991) 435.
- [25] P. Girard, J.L. Namy, H.B. Kagan, *J. Am. Chem. Soc.* 102 (1980) 2693.
- [26] K. Mashima, Y. Nakayama, A. Nakamura, N. Kanehisa, Y. Kai, H. Takaya, *J. Organomet. Chem.* 473 (1994) 85.
- [27] K. Mashima, H. Sugiyama, A. Nakamura, *Chem. Commun.* (1994) 1581.
- [28] D. Wilhelm, T. Clark, P.v.R. Schleyer, H. Dietrich, W. Mahdi, *J. Organomet. Chem.* 280 (1985) C6.
- [29] H. Yasuda, Y. Kajiwara, A. Nakamura, Conference Abstract in IX International Conference on Organometallic Chemistry, Dijon, 1979.
- [30] G. Erker, J. Wicher, K. Engel, F. Rosenfeldt, W. Dietrich, C. Krüger, *J. Am. Chem. Soc.* 102 (1980) 6344.
- [31] H. Yasuda, Y. Kajiwara, K. Mashima, K. Lee, A. Nakamura, *Chem. Lett.* (1981) 519.
- [32] U. Dorf, K. Engel, G. Erker, *Organometallics* 2 (1983) 462.
- [33] S.S. Wreford, J.F. Whitney, *Inorg. Chem.* 20 (1981) 3918.
- [34] Y. Kai, N. Kanehisa, K. Miki, N. Kasai, K. Mashima, K. Nagasuna, H. Yasuda, A. Nakamura, *J. Chem. Soc., Chem. Commun.* (1982) 191.
- [35] K. Tatsumi, H. Yasuda, A. Nakamura, *Isr. J. Chem.* 23 (1983) 145.
- [36] H. Yasuda, Y. Ohnuma, M. Yamauchi, H. Tani, A. Nakamura, *Bull. Chem. Soc. Jpn.* 52 (1979) 2036.
- [37] H. Yasuda, M. Yamauchi, Y. Ohnuma, A. Nakamura, *Bull. Chem. Soc. Jpn.* 54 (1981) 1481.
- [38] H. Yasuda, K. Nagasuna, M. Akita, K. Lee, A. Nakamura, *Organometallics* 3 (1984) 1470.

- [39] E.Y.X. Chen, R.E. Campbell Jr., D.D. Devore, D.P. Green, B. Link, J. Soto, D.R. Wilson, K.A. Abboud, *J. Am. Chem. Soc.* 126 (2004) 42.
- [40] H.C. Strauch, G. Erker, R. Fröhlich, *Organometallics* 17 (1998) 5746.
- [41] H.C. Strauch, G. Erker, R. Fröhlich, M. Nissinen, *Eur. J. Inorg. Chem.* (1999) 1453.
- [42] H.C. Strauch, R. Rössmann, S. Pacheiner, G. Erker, R. Fröhlich, B. Wibbeling, *J. Organomet. Chem.* 584 (1999) 318.
- [43] H.C. Strauch, G. Erker, R. Fröhlich, *J. Organomet. Chem.* 594 (2000) 388.
- [44] R.R. Schrock, *Acc. Chem. Res.* 12 (1979) 98.
- [45] J. Feldman, R.R. Schrock, *Prog. Inorg. Chem.* 39 (1991) 1.
- [46] R.D. Sanner, S.T. Carter, W.J. Bruton Jr., *J. Organomet. Chem.* 240 (1982) 157.
- [47] V.C. Gibson, J.E. Bercaw, W.J. Bruton Jr., R.D. Sanner, *Organometallics* 5 (1986) 976.
- [48] H. Yasuda, T. Okamoto, A. Nakamura, in: R.B. King, J.J. Eisch, (Eds.), *Organometallic Synthesis*, Elsevier, New York, 1988, vol. 4, p. 22.
- [49] J.M. Mayer, J.E. Bercaw, *J. Am. Chem. Soc.* 104 (1982) 2157.
- [50] G.P. Pez, *J. Chem. Soc., Chem. Commun.* (1977) 560.
- [51] G. Erker, K. Berg, C. Krüger, G. Müller, K. Angermund, R. Benn, G. Schroth, *Angew. Chem., Int. Ed. Engl.* 23 (1984) 455.
- [52] C. Sontag, H. Berke, C. Sarter, G. Erker, *Helv. Chim. Acta* 72 (1989) 1676.
- [53] J. Blenkins, H. de Liefde Meijer, J.H. Teuben, *Organometallics* 2 (1983) 1483.
- [54] J. Blenkins, B. Hessen, F. van Bolhuis, A.J. Wagner, J.H. Teuben, *Organometallics* 6 (1987) 459.
- [55] B. Hessen, F. van Bolhuis, J.H. Teuben, *Organometallics* 6 (1987) 1352.
- [56] B. Hessen, J. Blenkins, J.H. Teuben, G. Helgesson, S. Jagner, *Organometallics* 8 (1989) 830.
- [57] B. Hessen, J. Blenkins, J.H. Teuben, G. Helgesson, S. Jagner, *Organometallics* 8 (1989) 2809.
- [58] J. Chen, Y. Kai, N. Kasai, H. Yamamoto, H. Yasuda, A. Nakamura, *Chem. Lett.* (1987) 1545.
- [59] H. Yamamoto, H. Yasuda, K. Tatsumi, K. Lee, A. Nakamura, J. Chen, Y. Kai, N. Kasai, *Organometallics* 8 (1989) 105.
- [60] T. Okamoto, H. Yasuda, A. Nakamura, Y. Kai, N. Kanehisa, N. Kasai, *J. Am. Chem. Soc.* 110 (1988) 5008.
- [61] H. Yasuda, K. Tatsumi, T. Okamoto, K. Mashima, K. Lee, A. Nakamura, Y. Kai, N. Kanehisa, N. Kasai, *J. Am. Chem. Soc.* 107 (1985) 2410.
- [62] T. Okamoto, H. Yasuda, A. Nakamura, Y. Kai, N. Kanehisa, N. Kasai, *Organometallics* 7 (1988) 2266.
- [63] G.E. Herberich, U. Englert, P. Roos, *Chem. Ber.* 124 (1991) 2663.
- [64] G.E. Herberich, U. Englert, K. Linn, P. Ross, J. Runsink, *Chem. Ber.* 124 (1991) 975.
- [65] E. Melendez, A.M. Arif, A.L. Rheingold, R.D. Ernst, *J. Am. Chem. Soc.* 110 (1988) 8703.
- [66] L.-S. Wang, J.C. Fettinger, R. Poli, *J. Am. Chem. Soc.* 119 (1997) 4453.
- [67] R. Poli, L.-S. Wang, *J. Am. Chem. Soc.* 120 (1998) 2831.
- [68] L.-S. Wang, J.C. Fettinger, R. Poli, R. Meunier-Prest, *Organometallics* 17 (1998) 2692.
- [69] Y. Nakayama, H. Saito, N. Ueyama, A. Nakamura, *J. Organomet. Chem.* 627 (2001) 221.
- [70] W.A. Herrmann, R.A. Fischer, E. Herdtweck, *Organometallics* 8 (1989) 2821.
- [71] D.J. Beetstra, A. Meetsma, B. Hessen, J.H. Teuben, *Organometallics* 22 (2003) 4372.
- [72] A. Nakamura, unpublished results.
- [73] M. Dahlmann, G. Erker, R. Fröhlich, O. Mayer, *Organometallics* 18 (1999) 4459.
- [74] S. Takeda, H. Fukumoto, K. Mashima, K. Yamaguchi, A. Nakamura, *J. Phys. Chem.* 101 (1997) 278.
- [75] K. Mashima, S. Fujikawa, A. Nakamura, *J. Am. Chem. Soc.* 115 (1993) 10990.
- [76] K. Mashima, S. Fujikawa, H. Urata, E. Tanaka, A. Nakamura, *Chem. Commun.* (1994) 1623.
- [77] K. Mashima, S. Fujikawa, Y. Tanaka, Y. Urata, T. Oshiki, E. Tanaka, A. Nakamura, *Organometallics* 14 (1995) 2633.
- [78] E.L. Grogne, R. Poli, *Chem. Eur. J.* 7 (2001) 4572.
- [79] A.J. Sillanpaa, K.E. Laasonen, *Organometallics* 20 (2001) 1334.
- [80] K. Mashima, Y. Tanaka, A. Nakamura, *J. Organomet. Chem.* 502 (1995) 19.
- [81] K. Mashima, Y. Tanaka, M. Kaidzu, A. Nakamura, *Organometallics* 15 (1996) 2431.
- [82] K. Mashima, M. Kaidzu, Y. Nakayama, A. Nakamura, *Organometallics* 16 (1997) 1345.
- [83] K. Mashima, M. Kaidzu, Y. Tanaka, Y. Nakayama, A. Nakamura, J.G. Hamilton, J.J. Rooney, *Organometallics* 17 (1998) 4183.
- [84] K. Mashima, Y. Tanaka, A. Nakamura, *Organometallics* 14 (1995) 5642.
- [85] N. Xiao, B. Wang, J. Yin, Q. Xu, N. Tsumori, J. Sun, J. Chen, *Organometallics* 23 (2004) 257.
- [86] H. Yasuda, Y. Kajiwara, K. Mashima, K. Nagasuna, A. Nakamura, *Chem. Lett.* (1981) 671.
- [87] H. Yasuda, Y. Kajiwara, K. Nagasuna, K. Mashima, A. Nakamura, *Chem. Lett.* (1981) 719.
- [88] Y. Kai, N. Kanehisa, K. Miki, N. Kasai, M. Akita, H. Yasuda, A. Nakamura, *Bull. Chem. Soc. Jpn.* 56 (1983) 3735.
- [89] H. Yasuda, T. Okamoto, K. Mashima, A. Nakamura, *J. Organomet. Chem.* 363 (1989) 61.
- [90] H. Yasuda, T. Okamoto, Y. Matsuoka, A. Nakamura, Y. Kai, N. Kanehisa, N. Kasai, *Organometallics* 8 (1989) 1139.
- [91] G. Erker, K. Engel, U. Dorf, J. Atwood, W.E. Hunter, *Angew. Chem., Int. Ed. Engl.* 21 (1982) 914.
- [92] G. Erker, K. Engel, J.L. Atwood, W.E. Hunter, *Angew. Chem., Int. Ed. Engl.* 22 (1983) 494.
- [93] G. Erker, U. Dorf, *Angew. Chem., Int. Ed. Engl.* 22 (1983) 777.
- [94] G. Erker, F. Sosna, R. Zwtetler, C. Krüger, *Organometallics* 8 (1989) 450.
- [95] M. Akita, H. Yasuda, H. Yamamoto, A. Nakamura, *Polyhedron* 10 (1991) 1.
- [96] B. Temme, G. Erker, J. Karl, H. Luftmann, R. Fröhlich, S. Kotila, *Angew. Chem., Int. Ed. Engl.* 34 (1995) 1755.
- [97] D.D. Devore, F.J. Timmers, D.L. Hasha, R.K. Rosen, T.J. Marks, P.A. Deck, C.L. Stern, *Organometallics* 14 (1995) 3132.
- [98] S. Otsuka, T. Yoshida, A. Nakamura, *Inorg. Chem.* 6 (1967) 20.
- [99] K. Tatsumi, J. Takeda, Y. Sekiguchi, M. Kohsaka, A. Nakamura, *Angew. Chem., Int. Ed. Engl.* 24 (1985) 332.
- [100] K. Tatsumi, Y. Inoue, H. Kawaguchi, M. Kohsaka, A. Nakamura, R.E. Cramer, W. VanDoorne, G.J. Taogoshi, P.N. Richmann, *Organometallics* 12 (1993) 352.
- [101] K. Mashima, Y. Matsuo, S. Nakahara, K. Tani, *J. Organomet. Chem.* 593/594 (2000) 69.
- [102] Y. Matsuo, K. Mashima, K. Tani, *Bull. Chem. Soc. Jpn.* 75 (2002) 1291.
- [103] H. Kawaguchi, Y. Yamamoto, K. Asaoka, K. Tatsumi, *Organometallics* 17 (1998) 4380.
- [104] K. Mashima, Y. Matsuo, K. Tani, *Chem. Lett.* (1997) 767.
- [105] K. Mashima, Y. Matsuo, K. Tani, *Organometallics* 18 (1999) 1471.
- [106] Y. Matsuo, K. Mashima, K. Tani, *Organometallics* 21 (2002) 138.
- [107] J. Scholz, M. Nolte, C. Krüger, *Chem. Ber.* 126 (1993) 803.
- [108] B. Richter, J. Scholz, J. Sieler, K.-H. Thiele, *Angew. Chem., Int. Ed. Engl.* 34 (1995) 2649.

- [109] S. Kahlert, H. Görls, J. Scholz, *Angew. Chem. Int. Ed.* 37 (1998) 1857.
- [110] T. Spaniel, H. Görls, J. Scholz, *Angew. Chem., Int. Ed.* 37 (1998) 1862.
- [111] J. Scholz, S. Kahlert, H. Görls, *Organometallics* 17 (1998) 2876.
- [112] J. Scholz, H. Görls, H. Schumann, R. Weimann, *Organometallics* 20 (2001) 4394.
- [113] J. Scholz, G.A. Hadi, K.-H. Thiele, H. Görls, R. Weimann, H. Schumann, J. Sieler, *J. Organomet. Chem.* 626 (2001) 243.
- [114] J. Scholz, H. Görls, *Polyhedron* 21 (2002) 305.
- [115] J. Scholz, H. Görls, *J. Organomet. Chem.* 648 (2002) 87.
- [116] J. Scholz, H. Görls, *Organometallics* 23 (2004) 320.
- [117] H. Yasuda, E. Ihara, *Adv. Polym. Sci.* 133 (1997) 53.
- [118] H. Yasuda, Y. Yamamoto, K. Yokota, S. Miyake, A. Nakamura, *J. Am. Chem. Soc.* 114 (1992) 4908.
- [119] H. Yasuda, M. Furo, H. Yamamoto, A. Nakamura, S. Miyake, N. Kibino, *Macromolecules* 25 (1992) 5115.
- [120] Y. Matsuo, K. Mashima, K. Tani, *Angew. Chem. Int. Ed.* 40 (2001) 960.
- [121] A. Nakamura, N. Ueyama, K. Yamaguchi (Eds.), *Organometallic Conjugation*, Kodansha, Springer, 2002.