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Diene complexes of transition metals

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Prologue

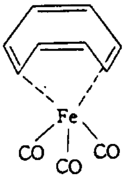
When I entered the Chemistry Department of Osaka University in 1955, organotransition-metal chemistry was in its early days. A literature survey on metallocenes was presented at a departmental colloquium, and organometallic catalysis of Ziegler–Natta and anionic polymerizations was about to be studied.

I was interested in the chemistry of coordination compounds and also in polymer chemistry. I chose to study at the Institute of Scientific and Industrial Research (ISIR), Osaka University, where Professor N. Hagihara had been investigating the Reppe reaction, e.g., acetylene cyclotetramerization. Dr. Hiroshi Yamazaki (now at RIKEN) was studying the mechanism of this reaction as a graduate student under Professor Hagihara. At that time, Professor Hagihara had the idea of cleaving cyclooctatetraene with an appropriate metal species into two molecules of cyclobutadiene complexes. The papers of H.C. Longuett-Higgins, L.E. Orgel, E.O. Fischer, and G. Wilkinson provided an impetus for his idea [1]. During my period of graduate research, early papers by P.L. Pauson and by R. Pettit introduced us to stable diene complexes of iron carbonyls [2].

There seemed a possibility of cleaving cyclooctatetraene (COT) into cyclobutadiene by complexation with an iron carbonyl group. We were fortunately in a position to have available sufficient amounts of COT and iron pentacarbonyl, since both of these had been used in the previous studies on the Reppe synthesis.

Cyclooctatetraene complexes of iron and cobalt

The first attempt to release COT was made in April, 1959, and involved heating the COT and iron pentacarbonyl together in refluxing xylene under nitrogen. A color change to deep red was observed, and I obtained nice red crystals of a complex. Professor Hagihara immediately asked me whether or not the complex was a known compound of iron and CO. The analysis posed difficulties since the volatility of the complex resulted in some damage to the combustion analysis apparatus. However, the analytical data clearly showed it to be $Fe(CO)_3(C_8H_8)$ (**1**) Although this was not the cyclobutadiene complex we were seeking, we were very glad to have obtained a new organometallic complex. The ^1H NMR data (40 MHz in cyclohexane) showed one singlet for the C_8H_8 protons. This implies fluxional behavior if the COT is bound in η^4-manner. Application of the 18-electron rule showed the complex to involve diene–metal coordination, and so I initially proposed a structure **1** similar to that of the COD complexes [3].



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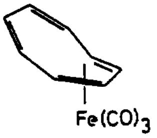

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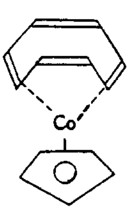
After submission of our paper in April, 1959, to the *Bulletin of the Chemical Society of Japan*, Professor Hagihara noticed a report by T.A. Manuel and F.G.A. Stone of the preparation of the same compound in the *Proceedings of the Chemical Society*, which had just arrived [4]. Manuel and Stone suggested a planar C_8H_8 ligand with some aromatic nature. Later in 1959, we saw a paper by M.D. Rausch and G.N. Schrauzer on the same complex prepared similarly [5].

Our original proposal was later found not to be correct, since X-ray crystallographical determination of its solid state structure by Professor W.N. Lipscomb revealed the unique 1,3-diene–iron structure **2** [6].

Since the 18-electron rule also predicted the existence of another class of diene complexes, CpCo(diene), I examined the thermal reaction of $CpCo(CO)_2$ with COT or COD in order to make the first such complexes. The complex $CpCo(C_8H_8)$ was judged to have the 1,2η : 5,6η-structure, **3**, by analysis of its ^{1}H NMR spectrum at 40 MHz [7]. The related diene complexes, **4** and **5**, were prepared similarly.



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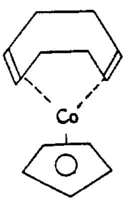

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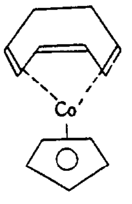

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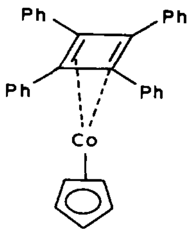
The reactions of these new diene complexes with $PhC{\equiv}CPh$ at 140 °C were investigated in order to find an effective route to the tetraphenylcyclobutadiene (TPCB) CpCo complex **6**. The presence of the TPCB ligand was confirmed by reductive cleavage to $(PhCH_2\text{-}CHPh)_2$ and by preparation of a CpCo complex, **7**, of 1,2,3,4-tetraphenylbutadiene by an independent route from $CpCo(C_5H_6)$ and Ph_2C_2 [8]. Since these reactivity studies suggested the intermediacy of metallacyclopentadiene complexes, the reaction of **1** with $PhC{\equiv}CPh$ was examined at 190 °C and found to give a stable TPCB-iron(0) complex, $Fe(C_4Ph_4)(CO)_3$. Thus, a mechanism involving σ–π rearrangement for the formation of TPCB complexes was proposed, in 1962 [9]. The validity of this mechanism was later confirmed by Dr. H. Yamazaki and Professor N. Hagihara by the thermal conversion (200 °C) of a cobaltacyclopentadiene complex, $CpCo(C_4Ph_4)(PPh_3)$, into $CpCoC_4Ph_4$ [10].

Starting in 1962, I spent one year as a post-doctoral fellow with Dr. M. Tsutsui of New York University in the Bronx. My aim was to make π-complexes with



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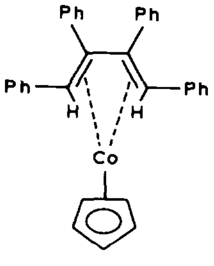

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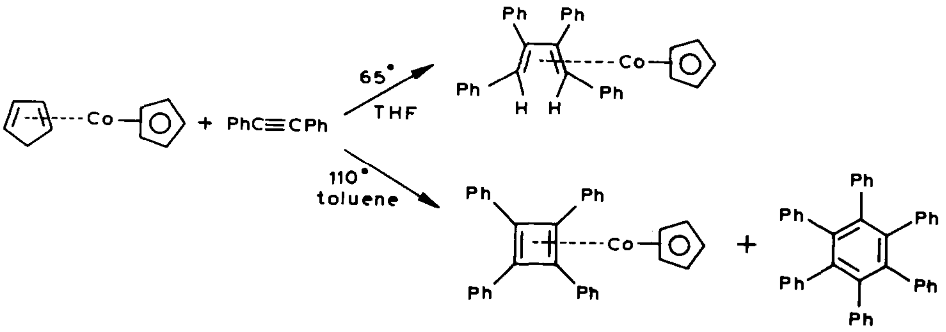


biologically active materials, and tricarbonyliron complexes of Vitamin A acetate and acetylergosterol were prepared [11]. These complexes involve stable diene–iron coordination and so were tested for possible medical effects, but without any positive results. A labilizing influence of iron(0) complexation on the neighboring acetoxy group was noted but no further work was carried out along this line.

Cumulene complexes

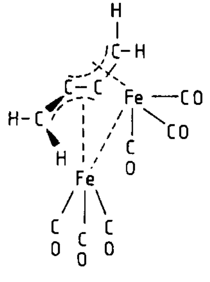
Cumulated dienes, and trienes attracted my attention when I returned to Japan in 1963. Professor Hagihara was interested at that time in ferrocenylpolyenes as potential materials for semiconductors and in preparing a series of such polyenes with the help of Dr. K. Sonogashira (now Professor at Osaka City University). Thus differocenylbutatriene was prepared by Dr. P.J. Kim (then a graduate student) together with its phenyl analogs [12]. I examined the π-complexation of tetraphenylallene and tetraphenylbutatriene with iron carbonyl species, and isolated quite stable mono- and di-iron complexes [13,15].

Since unsubstituted butatriene has only a transient existence, in situ debromination with zinc in the presence of $Fe_3(CO)_{12}$ was used to produce an analogous $Fe_2(CO)_6$ complex, **8** [13,14]. An iron complex of hexapentaene was prepared similarly in low yields [14] and assigned a composition, $C_6H_4Fe_3(CO)_{7-8}$, by elemental analysis. However, the composition was recently shown to be $C_6H_4Fe_4(CO)_{12}$ by Professors M. Oda and M. Iyoda of Osaka University, and the two isomers were shown to involve unique penta-coordinate carbons.

$$Ph_2C{=}C{=}CPh_2 + Fe(CO)_5 \xrightarrow{heat} Fe(CO)_3(Ph_2C{=}C{=}CPh_2)$$

$$Ph_2C{=}C{=}C{=}CPh_2 + Fe(CO)_5 \xrightarrow{heat} Fe_2(CO)_5(Ph_2C{=}C{=}C{=}CPh_2)$$

$$BrCH_2C{\equiv}CCH_2Br + Zn + Fe_3(CO)_{12} \longrightarrow$$



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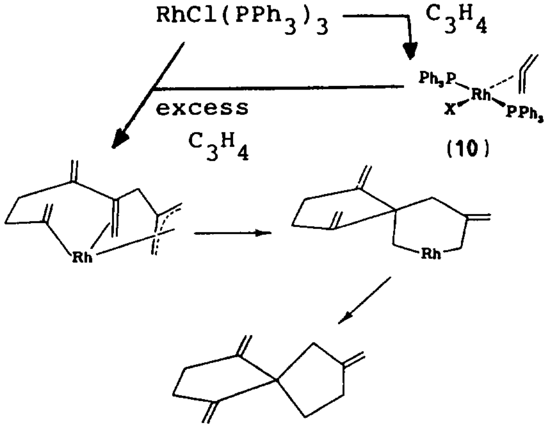
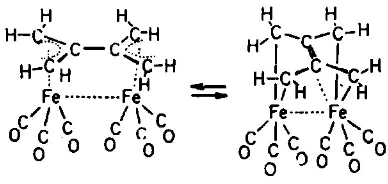
Complex formation of propadiene and propadiene polymers

The reaction of propadiene (allene) with iron or cobalt carbonyls was examined in 1964 and found to give a complex containing allene dimer, $Fe_2(CO)_6(C_6H_9)$ (**9**), a tetramethyleneethane complex with a fluxional structure and a dinuclear cobalt complex, $Co_2(CO)_6(C_3H_4)$ [16]. While these preparations were in progress, I was promoted in 1965 to an Associate Professorship in the Department of Chemistry, Faculty of Engineering Science, Osaka University, and began to collaborate with Professor Sei Otsuka. In the early part of this collaboration I was interested in allene and heterodiene complexes of late transition metals. Since the quasi-regular polymerization of allene had been observed earlier in catalysis by some organo-nickel complexes [17], I decided to study complex formation with platinum-group metals, with the help of Dr. K. Tani (now an Associate Professor at Osaka University). Monoallene complexes of Pt(0), $(PPh_3)_2Pt(allene)$, and Rh(I), $RhX(PPh_3)_2(allene)$ (**10**), were prepared, and found to involve η^2-coordination [19].





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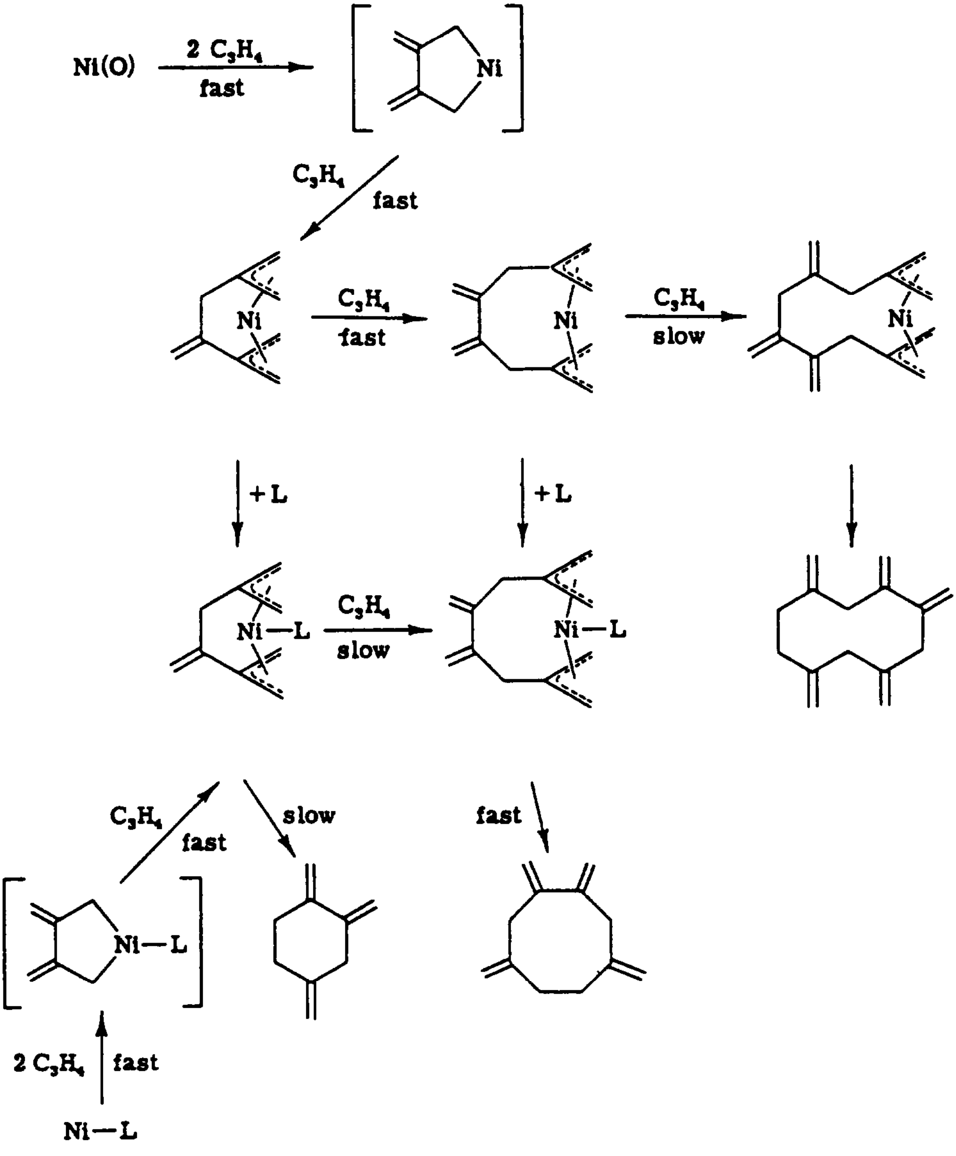
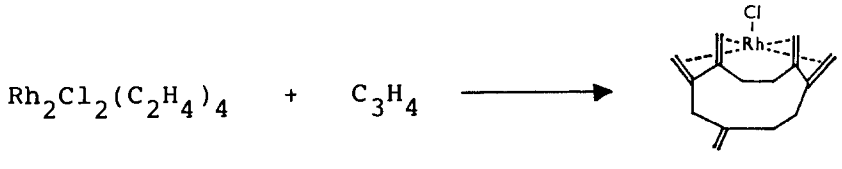


Fig. 1. Proposed mechanisms for catalysis in allene cyclo-oligomerization with Ni(0) species.

In some cases, propadiene oligomerization took place, catalytically or stoichiometrically. For example, nickel(0)- or rhodium(I)-catalyzed selective cyclotetramerization and cyclopentamerization of propadiene were observed [18] (see Fig. 1).

A Rh complex containing a different allene pentamer was isolated from the reaction of $[RhCl(C_2H_4)_2]_2$ with an excess of allene [19]. Allene-trimer complexes of iron carbonyl species were also prepared, as shown below [20].

High polymerization of allene to highly regular 1,2-polymers was achieved in catalysis by Co(I) or Rh(I) complexes [21]. In particular, $CoCl(PPh_3)_3$ was found to be highly active in aqueous emulsion systems, toluene/water/$CoCl(PPh_3)_3$, at



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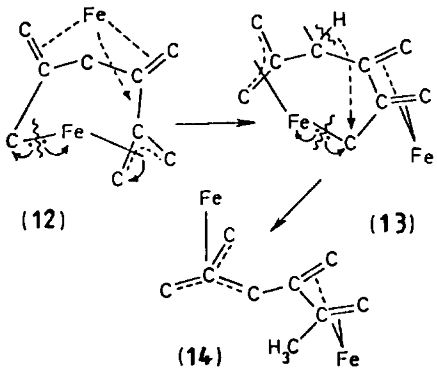
$$Fe_3(CO)_{12} + C_3H_4 \longrightarrow Fe_2(CO)_6(C_9H_{12}) \quad (12)-(14)$$

proposed mechanism for thermal transformation:



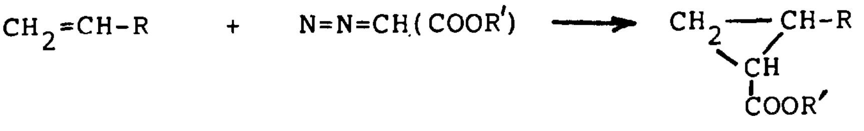
(12) (13) (14)

0 ° C, and to give crystalline polymers with a regular head-to-tail structure. Some Rh(I) catalysts, e.g. $[RhCl(CO)(PPh_3)]_2$, were active at room temperature in wet ethanol. These catalysts remain the best among the many used to give regular allene polymers.

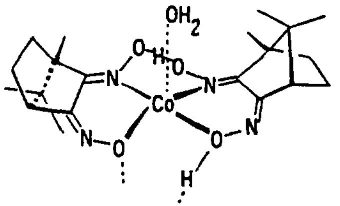
Heterodiene complexes

Azadiene, diazadiene, and tetrazadiene were the targets of my preparative efforts in 1965–1970 in collaboration with Professor S. Otsuka and Dr. T. Yoshida (now Professor at Osaka Prefectural University); a few examples of the complexes obtained are the following [22]: $(CH_3CH{=}CHCH{=}NC_4H_9)Fe(CO)_3$, $CH_2{=}C(CH_3)N{=}NCH_3Fe_2(CO)_6$ $(PhN{=}C(CH_3)C(CH_3){=}NPh)Fe(CO)_3$, and $(Ph{-}N{=}NN{=}NPh)CoC_5H_5$.

Heterocumulenes, such as $Ph_2C{=}C{=}NR$, PhN_3, and N_2CHCO_2R, were also used for complex formation, and the complexes $(Ph_2C{=}C{=}NR)Fe_2(CO)_6$ and (diazofluorene)$Ni(PR_3)_2$ were characterized [23]. During this preparative work we benefitted from experimental assistance by Dr. Y. Tatsuno, and the ability of a $Ni(CNtBu)_2$ fragment to form η^2-type complexes was demonstrated. Small molecules, such as O_2, azobenzene, diazoalkane, acetylenes, and electron-deficient olefins, were mostly found to give complexes with $Ni(CNBu)_2$ [24]. Systematic structural characterization of these complexes was carried out with the cooperation of Profes-



structure of Co(cqd)$_2$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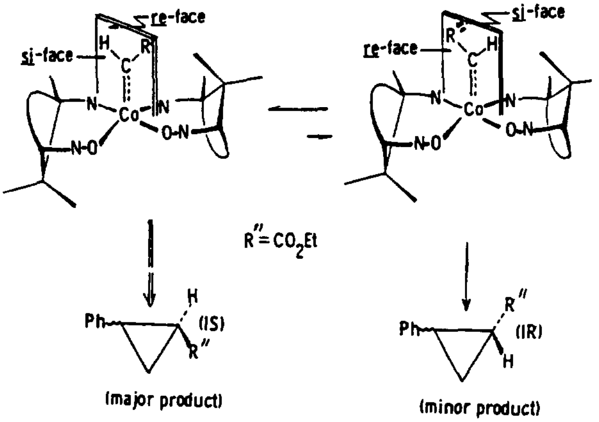
enantioselectivity mechanism



sor Jim Ibers (Northwestern University) and a very interesting "interligand-angle effect" related to the π-acidity of the η^2-ligand was observed [25]. Theoretical analysis of this inter-ligand angle effect was carried out with the help of Dr. K. Tatsumi (a graduate student in Professor T. Fueno's Laboratory at that time) [25]. An ^{18}O-isotopic infrared study of various O_2-complexes gave M–O_2 stretching force constants for the first time [26].

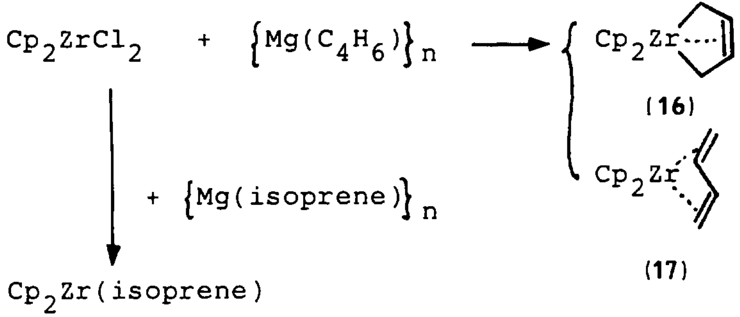
Catalytic decomposition of diazoalkanes was found to occur in the presence of Ni(0)–tert-phosphine complexes or bis(dioximato)cobalt(II) complexes [27]. Thus, a series of alkyl diazoacetates was allowed to react with styrene by catalysis of bis(camphorquinonedioximato)cobalt, **15**, to give mixtures of *cis*- and *trans*-phenylcyclopropanecarboxylates with high enantioselectivity [27]. Among four possible geometric isomers of the camphorquinonedioximato (cqd) ligands the *syn,anti*-isomer (previously designated as α-isomer) gave the best results as regards asymmetric yield. This remarkable finding was rationalized in terms of the unique steric disposition of the two cqd ligands around the cobalt center.

The steric congestion caused by the dimethylmethylene bridge in the cqd ligand was judged to be the most important factor in the enantioselectivity observed in the bond-forming process between cobalt-carbene species and styrene [28].

Diene complexes of early transition metals

Low-valent titanium halides activated by alkylaluminum reagents are well known to catalyze oligomerization and polymerization of 1,3-dienes. No discrete diene complexes have been isolated with $TiCl_2$ or similar metal species. When the chloro ligands were replaced by cyclopentadienyl, the compounds titanocene, $TiCp_2$, or zirconocene, $ZrCp_2$, were also found to be highly reactive and to have a transient existence when suitable donor ligands are absent.

When I moved as Professor to the Department of Macromolecular Science, Osaka University, in 1977, Dr. H. Yasuda had been studying the structures and reactions of the "magnesium–butadiene" adduct", $Mg(C_4H_6)$ and "magnesium–isoprene adduct", $Mg(C_5H_8)$, both of which can be readily prepared by his novel method [29]. He has a remarkable ability to prepare highly reactive organometallic compounds, and had been investigating organometallic initiators for polar monomers and conjugated dienes. I suggested to him in 1978 that he should try the reaction of the magnesium reagents with some transition metal halides, and in this way Cp_2Zr(isoprene) was obtained as air-sensitive red crystals from Cp_2ZrCl_2. The corresponding butadiene–Zr and –Hf complexes were also prepared. We described these Zr complexes at the International Conference of Organometallic Chemistry in 1979 [30]. A rich chemistry of early transition metal diene complexes was expected. The following year, we were surprised to see a communication by Professor Erker that reported a complex between *s-trans*-butadiene and Cp_2Zr [31]. His group prepared the *s-trans*-isomer by photolysis of Cp_2ZrPh_2 in the presence of butadiene. We thus examined more closely our butadiene–Zr complex obtained by the Mg method, and found the *s-trans*-isomer also to be present in it.



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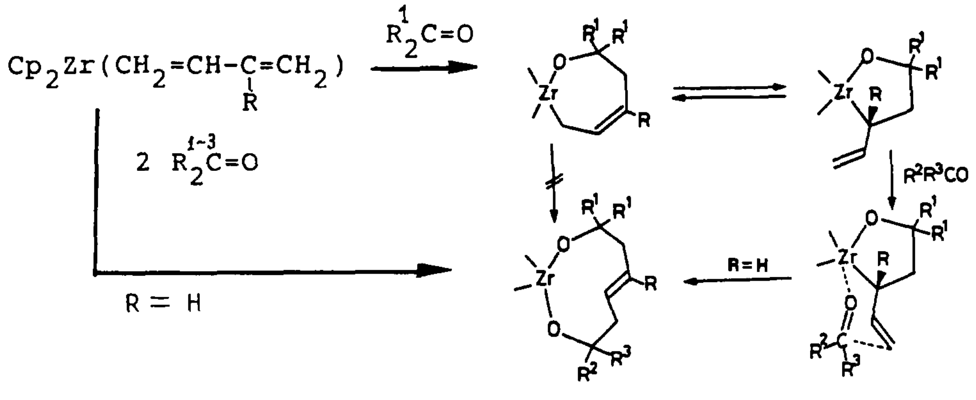
(17)

Since our method was found to give the isoprene complex (*s-cis* isomer only) readily, we concentrated on investigating its reactivity with a variety of unsaturated compounds [32]. Professor Yasuda examined the reaction with ketones on the basis of his experience with similar reactions of the magnesium–diene adduct. Facile insertion of ketones or other organic carbonyl compounds into one of the terminal diene–Zr bonds was observed, and the structure of the product was verified by an X-ray study [33]. Remarkable regioselectivity in this exclusive mono-insertion was noted in the case of the isoprene complex even with an excess of the ketone. The butadiene complex was found to react with one or two equivalents of aldehydes or ketones to give mono- or bis-insertion complexes, respectively. On protolytic demetallation these gave good yields of unsaturated alcohols with a *trans* double bond [33].

The Zr–diene complexes were found to take up olefins or dienes in stoichiometric reactions at somewhat higher temperature (~ 50 °C) to give novel metallacyclic complexes (**18**, **19**) containing η-allyl– and alkyl–Zr bonds [34]. The mechanism of this diene–olefin coupling reaction is considered to involve formation of a reactive mono-η^2-diene species (16-e species) from the *s-trans*- or the *s-cis*-diene complexes; the 16-e species then undergoes addition of an olefin to give a bis(olefin)zirconium

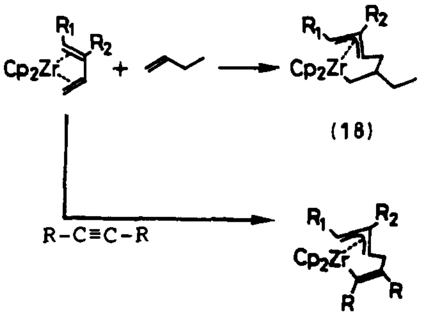


species, which cyclizes to a zirconacyclopentane species.

The reactivity of the Zr–diene complexes was explored in reactions with an extensive series of unsaturated compounds, including various heterocumulenes and heterodienes [43]. The reactions generally proceed almost quantitatively and selectively, and give various substituted zirconacycles that liberate unsaturated organic compounds in good yields [34].

Exact structure of the *s-trans* mode of diene coordination was clarified by an X-ray diffraction study of Cp_2Zr(1,4-diphenylbutadiene), which exists exclusively with the *s-trans* structure at the diene [35]. Professor N. Kasai and Dr. Y. Kai (both at Osaka University) cooperated with our group in this and many other X-ray structural determinations. They found that the two double bonds in the *s-trans*-diene complex coordinate to Zr in a uniquely distorted manner. This deformation at the diene is thought to arise from maximization of the overlap of the relevant π-orbitals.

The nature of bonding in the *s-cis-* and the *s-trans*-diene coordination was also analyzed in collaboration with Dr. K. Tatsumi (Osaka University) who used the EHMO approach. His analysis clearly showed unique diene bonding for the *s-cis*-isomer and also for the *s-trans*-isomer. The former is better described as a zirconacyclopentene complex and the latter as a bis(olefin)zirconium complex [36].



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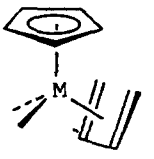
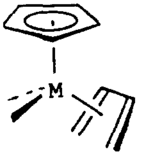
The analysis (by Professor Yasuda) of NMR parameters, e.g. ^1J(C–H) and ^3J(H–H), also supported these descriptions [37].

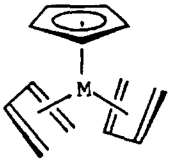
The magnesium–diene reagent, more correctly called endiylmagnesium bis(tetrahydrofuranate), was subsequently utilized by many chemists around the world. The preparations of tris(diene)tungsten, carbonylbis(diene)manganese, and $Cp_2^{\star}$Th(diene) provide examples [38]. With the help of Dr. T. Okamoto (a graduate student at that time), we also prepared mono- and bis-(diene) complexes of niobium and tantalum [39]. The orientation of the two diene ligands relative to the cyclopentadienyl ligand in these bis(diene) complexes was found to be characteristic for early transition metals. Thus, a novel supine/prone designation was devised by Professor Yasuda to indicate the unique geometry of diene coordination in this type of complexes with the general formulation CpM(L)$_n$(diene); L = mono- or bi-dentate ligand. These designations are frequently used to indicate the geometry of a diene ligand in some Mo and Re complexes.



supine
isomer



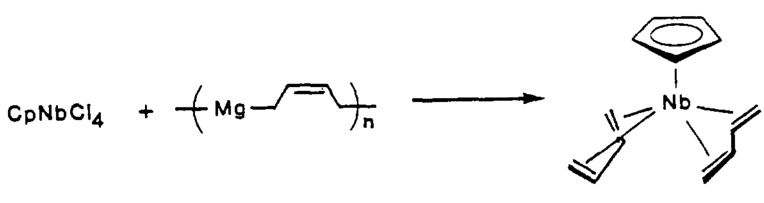
prone
isomer



supine-prone
isomer

The electronic reasons for favoring the unique supine–prone-orientation of two diene ligands in CpTa(C_4H_6)$_2$ were elucidated by Dr. K. Tatsumi through EHMO calculations [39]. A detailed analysis of structural parameters based on X-ray structural studies (by Professors Kai and Kasai) was carried out, and revealed the differences in the nature of metal–diene bonding between the supine and prone orientations [39]. Thus, the supine diene ligand was found to have an enhanced metallacyclic character relative to the prone ligand. This conclusion was also supported by EHMO calculations made by Dr. Tatsumi [39].

Niobium analogs of the bis(diene) complexes involving 2,3-dimethylbutadiene were also found to have such supine–prone structures [42]. In the case of butadiene, however, the samples of CpNb(C_4H_6)$_2$, prepared from $CpNbCl_4$ and Mg(C_4H_6), were found by careful analysis of the ^{1}H NMR spectra at 500 MHz to be inseparable mixtures of a bis(*s-cis*)-supine–prone-isomer and a (*s-cis*)(*s-trans*)-isomer (**20**). This is the first example of bis(diene) complexes with two different modes of coordination to the same metal.



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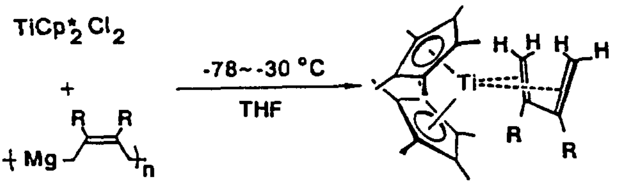
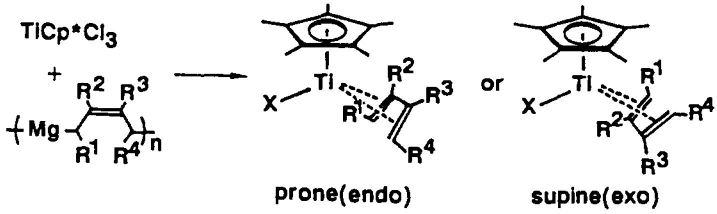


(21) R =H, R =CH$_3$
R =R =CH$_3$

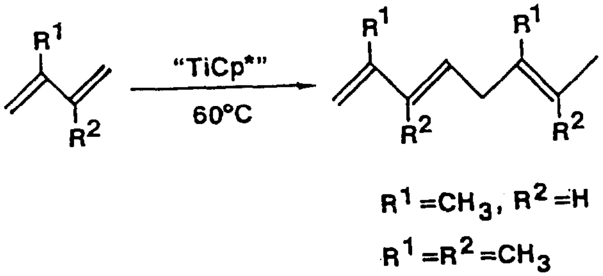


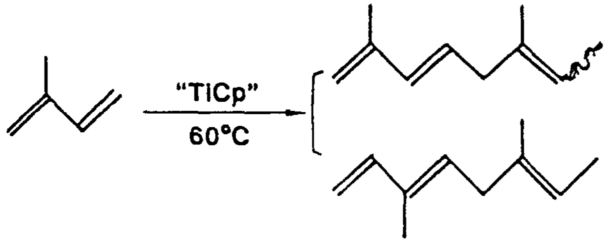
(22)

The Ti analog of the type Cp_2Ti(diene) was thermally more unstable than the corresponding Zr species, and so it was decided to enhance the thermal stability by using the C_5Me_5 ligands (Cp*). The reaction of $Cp_2^\star TiCl_2$ with $Mg(C_4H_6)$ was found to give $Cp_2^\star Ti$(*s-cis*-C_4H_6) (21) as a red solid, which was characterized by ^{1}H-NMR spectroscopy. Similarly, in 1986–1988, the reaction of $Cp^\star TiCl_3$ with a series of endiylmagnesium compounds was found to give $Cp^\star TiX$(diene), **22**, X = Cl, Br, I, in good yields [40]. These Ti–diene complexes were obtained during work carried out in collaboration with Professor Yasuda and Dr. Hitoshi Yamamoto (a graduate student at that time). The geometry of the diene ligand in $Cp^\star TiX$(diene) was revealed by X-ray studies and by NMR spectroscopy to be controlled by the positions of the substituents on the diene. Internal substitution gives rise to the supine isomer and terminal substitution results in the prone isomer. The nature of the Ti–C bonds was also examined by analysis of the NMR spectra, and an enhanced metallacyclopentene character was found for the supine isomer. Almost at the same time, analogous diene complexes of Zr and Hf were made by Prof. J.H. Teuben et al. [41].

Catalysis of diene complexes in diene oligomerization and polymerization

Most of the diene complexes of Group 4 and 5 metals were examined as catalysts for polymerization of dienes. Professor Yasuda's group (with Dr. T. Okamoto and Dr. H. Yamamoto) investigated this aspect. Thus, $CpNb(C_4H_6)_2$ was found to initiate linear polymerization of butadiene to 1,4-*trans*-rich polymers [42]. The same complex catalyzed linear dimerization of isoprene to a head-to-tail dimer [42]. Although $Cp^\star TiCl(C_4H_6)$ was inactive towards dienes, a mixture of $Cp^\star TiCl(C_4H_6)$ and an alkylating agent was found to be active in a highly selective head-to-tail dimerization of isoprene [40]. A similar Ti complex with a less bulky Cp ligand catalyzed formation of a head-to-head dimer of isoprene for the first time, in ca 50%





selectivity. Since complexes of the type CpTi(diene), are assumed to be active species, attempts to isolate them were made, but without success, and only ESR data are available for this formally Ti(I) species.

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For the enjoyment of organometallic chemistry I have experienced I wish to thank Professor N. Hagihara for introducing me to a rich field of organotransition metal chemistry during my first encounter with olefin–mercury complexes in 1956 as a student. I am indebted to the late Professor M. Tsutsui for my post-doctoral experience in the U.S.A, and also to Professor S. Otsuka for his collaboration during the period 1965–1977. A delightful collaboration with Professors T. Yoshida, K. Tani, H. Yasuda, Dr. Y. Tatsuno, and Dr. K. Tatsumi, is also highly appreciated. The continuing interest and cooperation of the Osaka University X-ray team, in particular Professor N. Kasai and Professor Y. Kai, are gratefully acknowledged. Finally I acknowledge the experimental work of many dedicated students, whose names appear in the references.

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Note added in proof. Professor H. Yasuda is now at the Department of Applied Chemistry, Faculty of Engineering, Hiroshima University.