Journal of Organometallic Chemistry, 428 (1992) 49–58
Elsevier Sequoia S.A., Lausanne
JOM 22361

Agostic interaction in early transition metal alkyls and their role in catalytic activity for olefin polymerizations *

Kazushi Mashima and Akira Nakamura

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560 (Japan)

(Received September 20, 1991)

Abstract

Trends in agostic interaction at the metal–carbon bond in early transition metal organometallic complexes are discussed in relation to the active species in catalytic oligomerization and polymerization of unsaturated hydrocarbons. Experimental results on some new organometallic complexes are combined with theoretical considerations in the search for new selective and homogeneous organometallic catalysts for polymerization and oligomerization.

Introduction

Organometallic derivatives of early transition metals such as alkyltitanium species have attracted much interest since the discovery of the Ziegler–Natta catalyst [1]. However, the high reactivity of such species and their heterogeneous nature have made it difficult to obtain basic information on their structure and properties. In recent years ligands such as pentamethylcyclopentadienyl (C_5Me_5) or bulky alkoxo ligands have begun to be exploited, so the previous situation has changed considerably and many new reactive early transition metal organometallic complexes are now known. Some of these, such as Kaminsky's catalyst systems which include oligomeric methylaluminoxane (MAO), have been found to initiate olefin polymerization that is highly stereospecific, with for instance a high degree of syndiotactic polymerization, and with hitherto unknown precision and activity [2]. Thus, bis(cyclopentadienyl)metal species (*e.g.* cationic Cp_2Zr–alkyl) have now become well known for their ability to produce polyolefins in high turnover [3]. The essential feature for the catalysis can be traced to the α-agostic interaction between metal and alkyl hydrogens. The extent and steric condition of the agostic

---

Correspondence to: Professor A. Nakamura, Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan.

* Dedicated to Professor A. Yamamoto upon his retirement from Tokyo Institute of Technology and in honour of his contribution to organometallic chemistry.

Table 1

α- and β-agostic interactions observed in early transition metal complexes

Complexes [a]	d(M–H) (Å)	Angle M–C–R, R = H or C_β (deg)	Method	Reference
α-interaction (R = H)				
$Ti(Me)Cl_3(dmpe)$	2.447(3)	93.5(2)	neutron	10, 11
$Ti(Me)Cl_3$	2.53	101(2)	neutron [b]	12
$Cp^*Ti(CH_2Ph)_3$	2.32 2.37	–	X-ray	13
$Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}CH_3)Pt(Me)(PMe_2Ph)$	1.93(5)	51.7(27)	X-ray	14
$Zr(CH_2SiMe_3)_4(dmpe)$	2.48	–	X-ray	15
$Cp_2Nb(Et)(2\text{-butyne})$	2.36(13)	79	X-ray	16b,c
$[C_5(^tBu)(CH_2{}^tBu)_2(CH_2CMe_2\overline{CH_2)_2]}TaCl_2$	2.30(8)	82(4)	X-ray	17
$Cp^*_2Th(CH_2CMe_3)_2$	2.597(9) 2.648(9)	84.4(5) 87.1(5)	neutron	8
β-interaction (R = C_β)				
$Ti(Et)Cl_3(dmpe)$	2.22(10)	86.3(6)	X-ray	10, 18
$[Cp_2Zr(Et)(PMe_3)]^+$	2.16	84.7(5)	X-ray	19
$Cp_2ZrCl(CH_2CH_2)RuCp(PMe_3)_2$	2.19(2)	82.5(6)	X-ray	20
$Cp_2ZrBr\{C(SiMe_3)=C(H)Ph\}$	2.19(5)	88.7(4)	X-ray	21
$[Tp'(CO)_2W=C(Ph)Me]^+$	–	91(1)	X-ray	22

[a] Cp = η^5-C_5H_5; Cp* = η^5-C_5Me_5, dmpe = $Me_2PCH_2CH_2PMe_2$; Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate. [b] Gas phase structure.

interaction have been considered very important for these active and selective olefin catalyses.

Theoretical investigation on the nature of metal–carbon bonding in these early transition metal complexes has been one of the targets of recent research in organometallic chemistry.

Nature of early transition metal alkyl bonds

Recently, specific interactions of various transition metals with α- or β-hydrogen atoms of the alkyl group have been observed [4]. Table 1 presents some examples from early transition metals, and here α-agostic interaction in some metal–alkyl complexes has been proposed as an important property for catalytically active species for olefin polymerization [5]. According to mechanisms proposed by earlier workers [6,7], during the propagation, a vacant site may be available in the catalyst before the alkene is coordinated to a monometallic active center. The α-hydrogen interaction gives the catalyst the properties of a resting state which readily receives coordination of alkene for successive insertion, while β-hydrogen interaction causes β-hydrogen elimination to give olefinic oligomers instead of high-molecular-weight polymers.

Some alkyl complexes of actinoids have been found on the basis of X-ray and neutron analysis to include α-agostic interactions, *e.g.* $Cp^*_2Th(CH_2CMe_3)_2$, where one alkyl group has a shortened M–C distance and a remarkably wide Th–Cα–Cβ angle (158°) [8]. An EH-MO calculation invoking relativistic Dirac–Fock functions for ethyl–lanthanoid and ethyl–actinoid bonds in Cp_2M–Et has indicated that

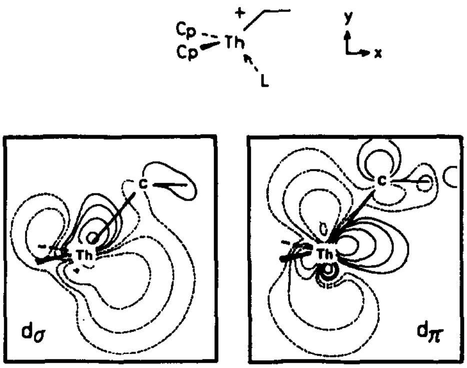


Fig. 1. Contour plots of the two frontier orbitals *dσ* and *dπ* of $[Cp_2Th(CH_2CH_3)]^+$ [9].

quasi-relativistic 6*d* and 5*f* orbitals were found to be important in α-agostic interactions with one of the ethyl groups of Cp_2ThEt_2 [9]. The origin of this specific α-agostic interaction may be traced to the shapes of the metal orbitals. Thus, the shape of vacant orbitals in Cp_2ThEt^+, as shown in Fig. 1, is much more diffuse than those of first row transition metals such as in Cp_2Fe. It is this characteristic shape that is believed to be the basis of the α-agostic interaction being preferred. Since β-agostic interaction leads to β-hydride elimination which terminates the growth of the polymer, favorable α-agostic interaction is vital for formation of polymers of high molecular weight with small polydispersities. Relevant examples of agostic alkyls are cited in Table 1. The geometric parameters indicate the profound influence of the identity of the metal and of the co-ligands.

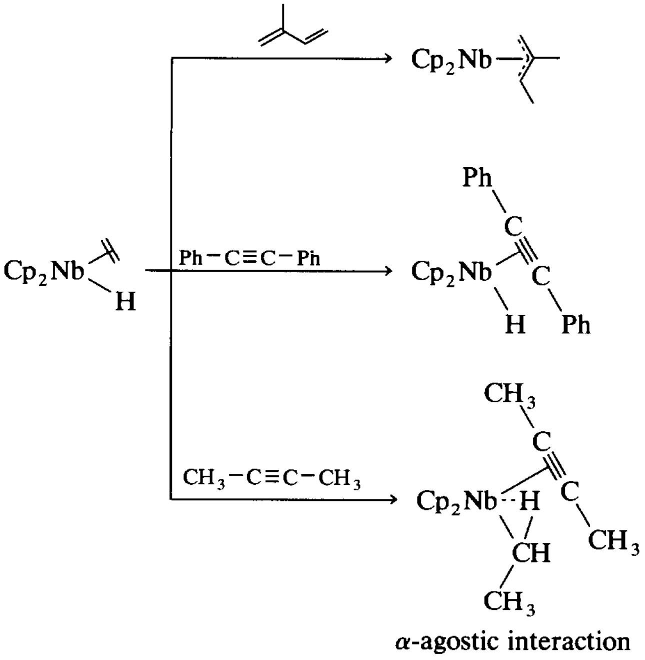
The stereoselectivity of the hydrocyclization of 1,5-hexadiene catalyzed by Cp^*_2ScH and of the hydrodimerization of 1-hexene catalyzed by zirconocene–MAO have been demonstrated by deuterium-label experiments [23,24], and α-agostic interaction was invoked as the cause. Thus, we expected that the cationic d^0 metallocene complexes of Group 4 metals and isoelectronic neutral lanthanoid complexes have unique α-agostic interactions, and these complexes have the capability to catalyze the polymerization of olefins.

The agostic interaction is generally caused by fairly strong electrophilicity at the metal. Usually, 14- or 16-electron configuration of the metal is required. The catalytically active species of group 3 and 4 metals are cited in Table 2 to illustrate this point. It is important that the species $[Cp_2MR]^{n+}$ ($n = 0, 1$) have 14-electron configurations and are thus ready to accept a 2-electron ligand to become a

Table 2

Comparison of active species, $[Cp_2MR]^{n+}$, for olefin insertion

Metals	Group 3 ($n = 0$)	Group 4 ($n = 1$)	Group 5 ($n = 0$)
Electron count (active species + olefin)	14+2	14+2	16+2
Lability or activity (catalytic)	+	+	−
Counter anion	no	yes	no
Strength of olefin coordination	weak	medium	strong



Scheme 1

somewhat more stable 16-electron species. On the other hand, Group 5 metal species of similar structure would have 16 electrons in the Cp_2MR state and 18 electrons in the Cp_2MR(olefin) state. Group 5 metals in the highly unusual dicationic $[Cp_2MR]^{2+}$ state would have 14 electrons.

Examples of the presumed active species, Cp_2MR(olefin), have already been prepared for M = Nb, Ta and have been found to be stable to further attack by olefins. A systematic investigation of their reactivity has shown that $Cp_2NbH(C_2H_4)$ reacts sluggishly with conjugated dienes or with substituted acetylenes at higher temperatures, *e.g.* 60–80°C [16]. Relevant examples are shown in Scheme 1.

Kinetic inertness of this type of 18-electron complex is thus well demonstrated. When their reaction with more highly π-acidic acetylenes was examined, elimination of ethylene resulted in a still more stable hydrido–acetylene complex, *e.g.* $Cp_2NbH(PhC{\equiv}CPh)$. In these cases, a 20-electron intermediate, $Cp_2NbH(C_2H_4)$-(acetylene), is postulated (similar 20-electron species are suggested for the reactions of Cp_2MoH_2 [25]).

The reaction with a disubstituted acetylene, such as $CH_3C{\equiv}CCH_3$, gave $Cp_2NbEt(CH_3C{\equiv}CCH_3)$, whose molecular structure has recently been shown to exhibit an interesting α-agostic interaction [16]. Combined steric crowding at the metal–ethyl site is the cause of the observed α-agostic interaction. When β-hydrogen is induced to interact with the metal, severe steric congestion due to the methyl group arises at coordinated 2-butyne. Since ethyl–metal species usually prefer β-agostic interaction, as observed for an ethyl complex of titanium, $TiCl_3Et$(dmpe) [10,18], the present observation shows the important tendency of

Table 3

NMR ^1J(C–H) values and structural data of ethylene coordinated to early transition metals

Complexes	Formal oxidation state	^1J(C–H)	M–C (Å)	C–C (Å)	Angle C–M–C (deg)	Reference
C_2H_4	–	165	–	1.337(2)	–	29
$Cp^*_2Ti(C_2H_4)$	2	145	2.160(4)	1.438(5)	38.9(1)	27
$Cp_2Zr(PMe_3)(C_2H_4)$	2	144	2.354(3) 2.332(4)	1.449(6)	36.0(1)	30
$Cp_2Nb(H)(C_2H_4)$	3	153 156				31
$Cp_2NbEt(C_2H_4)$	3	153 154.5	2.277(9) 2.320(9)	1.406(13)	35.6(3)	31
$Cp_2TaMe(C_2H_4)$	3	148 149				32
$Cp^*Ta(C_2H_4)Cl_2$	3	151				33
$TaCl_2(C_2H_4)(Et)(PMe_3)_2$	3	151				34
$TaCl_2(C_2H_4)(CH_2{}^tBu)(PMe_3)_2$	2	151				34
$WClMe(PMe_3)_2(C_2H_4)_2$	2	156				35
$WCl_2(PMe_3)_2(C_2H_4)_2$	2	155				35
$WMe(PMe_3)_2(C_2H_4)_2$-$(ClAlMe_xCl_{3-x})$	2	154	2.183(10) 2.169(9) 2.202(10) 2.174(10)	1.417(14) 1.428(14)	37.7(4) 38.4(4)	35

early transition metals to favor α-agostic interactions in the sterically crowded organometallic environment, which is important for successive insertion of olefin.

Effects of degree of C–C unsaturation on coordination to early transition metals

The nature of metal–olefin bonding has been explained in terms of synergic σ-donation and π-back-donation. As characterization of metal–olefin bonds in early transition metal complexes has progressed, the contributions of these components of bonding were found to depend upon the number and levels of *d*-electrons. Structural data and NMR studies have revealed the nature of the bonding [26]. In particular, bond lengths and angles around the coordinating unsaturation together with the NMR ^1J(C–H) values of the =C–H bonds have proved particularly important.

As shown in Table 3, the ^1J(C–H) values of C_2H_4 decrease on strong coordination to low-valent early transition metals. An approach to sp^3 hybridization is clearly shown. It was therefore concluded that in some early transition-metal complexes a low-valent metal binds olefin so strongly that no polymerization is possible. Some ethylene complexes have been regarded to have metallacyclopropane as a canonical form and concerted alkene insertion into strained metallacyclopropane to form metallacyclopentane has been observed [27,28]. Weaker olefin–metal interaction seems to be a requisite for catalytic polymerization where specific steric control is necessary for regularity and stereoselectivity.

Alkene coordinates only weakly to a mononuclear samarium complex. When one of the typical Group 3 metals such as Cp^*_2Sm is allowed to react with 1-alkenes, their allylic C–H bond is activated giving more stable allyl-type com-

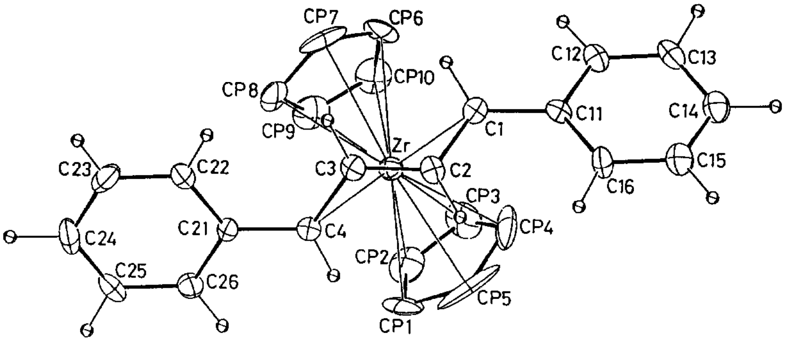
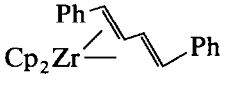


Fig. 2. Molecular structure of Cp_2Zr(*s-trans*-1,4-diphenyl-1,3-butadiene) [42a].

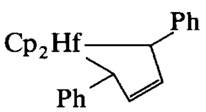
plexes, $Cp^*{}_2Sm(allyl{-}R)$ [36]. In the case of stilbene a dinuclear complex $[Cp^*{}_2Sm]_2$(stilbene) is produced [37]. On the other hand, thermally stable ethylene and 1-alkene complexes of Group 4 and 5 metals have been prepared without difficulty (Table 3).

In contrast to the low-valent transition metal complexes, organolanthanoids and -actinoids in oxidation states of +2 to +4 ($s^0d^0f^n$ configuration) bind acetylenes only weakly. Acetylene complexes of samarium and ytterbium, $[Cp^*{}_2Sm]_2(PhC{\equiv}C{-}C{\equiv}CPh)$ [38] and $Cp^*{}_2Yb(MeC{\equiv}CMe)$ (15e species) [39] have been prepared and the acetylene–samarium bonding in $Cp_2Sm(HC{\equiv}CH)$ has been analyzed by the EH-MO method [40]. The results indicated only weak bonding interaction with a slight change in the structure of acetylene by coordination. Absence of *d*-electrons from the orbital interaction is the most likely reason for the weakness.

Conjugated dienes generally coordinate more strongly to transition metals, particularly in the case of the low-valent early transition metals [41]. In some cases, the mode of their coordination is unique, *i.e.* the *s-trans* and metallacyclopentene types are frequently found as shown below and in Figs. 2 and 3 [42*,43]. A slight difference in the bonding characteristics, *e.g.* from zirconium to hafnium, is amplified to result in the change of diene coordination mode.



s-trans



s-cis or metallacyclopentene

Some examples of stereospecific polymerization of olefins and acetylenes by new organometallic complexes of early transition metals

To follow up these theoretical and physical investigations, we have studied the catalytic effects of mono- or bis-Cp derivatives of various early transition metals on ethylene, butadiene, and substituted acetylenes at 30–60°C. Ethylene was found to polymerize under the influence of $CpNbCl_4$ in the presence of MAO at 0°C [44].

Regarding 1,3-dienes, complexes such as Cp_2Zr(diene), $CpNb(diene)_2$ or $[CpNbCl(diene)]_2$ were found to be catalytically active for dimerization or polymer-

---

* Reference number with asterisk indicates a note in the list of references.

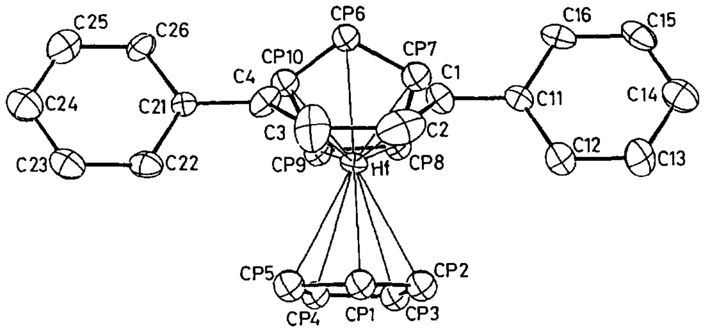
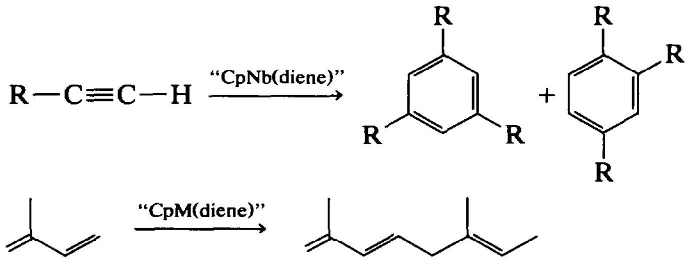


Fig. 3. Molecular structure of Cp_2Hf(*s-cis*-1,4-diphenyl-1,3-butadiene) [42b,43].

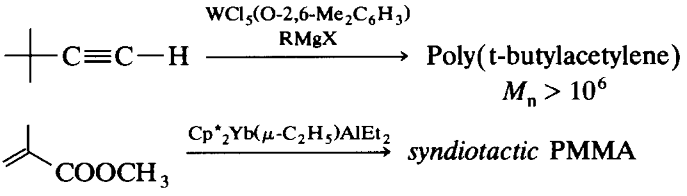
ization [41,45]. $CpNb(butadiene)_2$ polymerizes butadiene to 1,4-*trans* polymers at 60°C in toluene. $[CpNbCl(isoprene)]_2$ catalyzes head-to-tail dimerization (85% selectivity) of isoprene at 60°C. These Nb-diene complexes also promote cyclotrimerization of 1-alkynes. Bulky cyclopentadienyl ligands such as C_5Me_5 promote selectivity in dimerization of isoprene. Thus, Cp*TiCl(diene) activated with RMgX catalyzes head-to-tail coupling of isoprene in 99% selectivity at 60°C in benzene–THF [46]. These diene catalysts utilize selective C–C bond forming reactions at the monocyclopentadienyl–metal active sites where the two diene ligands are coupled through specific η^3-allyl intermediates.

Ethylene polymerization ($M_w > 10^6$) is also catalyzed by bulky phenoxides of Ti and Zr when mixed with an excess of MAO [40]. In the case of phenoxide complexes of Nb^V, and W^{VI}, efficient polymerization of t-butylacetylene was observed when activated with EtMgBr at 0–30°C to give high-molecular-weight polymers ($M_n = 10^5$–10^6) with narrow PDI [47]. $TiCl_3$(2,6-dimethylphenoxo) activated by t-BuMgCl catalytically cyclotrimerizes 1-butyne and linearly dimerizes 1-hexene at 60°C. Bis(pentamethylcyclopentadienyl) derivatives of lanthanoids are known for their activity in ethylene polymerization [48]. We have examined block co-polymerization of ethylene and MMA with a new binuclear complex, $Cp^*_2Yb(\mu\text{-}C_2H_5)AlEt_2$ [49]. The initial addition of ethylene was followed by addition of MMA in the presence of the above catalyst to give the co-polymer with syndiotactic PMMA chain [16c,50]. "Living" homopolymerization of MMA is also possible [16c,51].

We have demonstrated the importance of systematic research on the organometallic active species in the area of early transition metals and have suggested some future courses for such research.



Scheme 2



Scheme 3

References and notes

1 J. Boor, Jr., Ziegler–Natta Catalysts and Polymerizations, Academic Press, New York, 1979.

2 (a) H. Sinn and W. Kaminsky, Adv. Organometal. Chem., 18 (1980) 99; (b) W. Kaminsky, K. Kulper, H.-H. Brintzinger and F.R.W.P. Wild, Angew. Chem., Int. Ed. Engl., 24 (1985) 507; (c) J.A. Ewen, L. Haspeslagh, J.L. Atwood and H. Zhang, J. Am. Chem. Soc., 109 (1987) 6544; (d) J.A. Ewen, R.L. Jones and A. Razavi, J. Am. Chem. Soc., 110 (1988) 6255; (e) A. Grassi, A. Zamberi, L. Reconi, E. Albizzati and R. Mazzocchi, Macromolecules, 21 (1988) 617; (f) W. Roll, H.-H. Brintzinger, B. Rieger and R. Zolk, Angew. Chem., Int. Ed. Engl., 29 (1990) 279; (g) N. Piccolrovazzi, P. Pino, G. Consiglio, A. Sironi and M. Moret, Organometallics, 9 (1990) 3098; (h) L. Resconi and R.M. Waymouth, J. Am. Chem. Soc., 112 (1990) 4953; (i) D.T. Mallin, M.D. Rausch, Y.-G. Lin, S. Dong and J.C.W. Chien, J. Am. Chem. Soc., 112 (1990) 2030; (j) S. Collins, W.J. Gauthier, D.A. Holden, B.A. Kuntz, N.J. Taylor and D.G. Ward, Organometallics, 10 (1991) 2061; (k) T. Mise, A. Kageyama, S. Miya and H. Yamazaki, Chem. Lett., (1991) 1525, and references cited therein.

3 (a) J.J. Eisch, A.M. Piotrowski, S.K. Brownstein, E.J. Gabe and F.L. Lee, J. Am. Chem. Soc., 107 (1985) 7219; (b) R.F. Jordan, C.S. Bajgur, R. Willett and B. Scott, J. Am. Chem. Soc., 108 (1986) 7410; (c) M. Bochmann and L.M. Wilson, J. Chem. Soc., Chem. Commun., (1986) 1610; (d) M. Bochmann, L.M. Wilson, M.B. Hursthouse and R.L. Short, Organometallics, 6 (1987) 2556; (e) R.F. Jordan, C.S. Bajgur, W.E. Dasher and A.L. Rheingold, Organometallics, 6 (1987) 1041; (f) R.F. Jordan and S.F. Echols, Inorg. Chem., 26 (1987) 383; (g) R.F. Jordan, R.E. LaPointe, C.S. Bajgur, S.F. Echols and R. Willett, J. Am. Chem. Soc., 109 (1987) 4111; (h) Z. Lin, J.-F. Le Marechal, M. Sabat and T.J. Marks, J. Am. Chem. Soc., 109 (1987) 4127; (i) R. Taube and L. Krukowka, J. Organomet. Chem., 347 (1988) C9; (j) G.G. Hlatky, H.W. Turner and R.R. Eckman, J. Am. Chem. Soc., 111 (1989) 2728; (k) R.F. Jordan, R.F. LaPointe, P.K. Bradley and N. Baenziger, Organometallics, 8 (1989) 2829; (l) M. Bochmann, A.J. Jaggar and J.C. Nicholls, Angew. Chem., Int. Ed. Engl., 29 (1990) 780; (m) X. Yang, C.L. Stern and T.J. Marks, J. Am. Chem. Soc., 113 (1991) 3623.

4 M. Brookhart, M.L.H. Green and L.-L. Wong, Prog. Inorg. Chem., 36 (1988) 1.

5 M. Brookhart and M.L.H. Green, J. Organomet. Chem., 250 (1983) 395.

6 (a) P. Cossee, J. Catal., 3 (1964) 80; (b) E.J. Arlman, J. Catal., 3 (1964) 89; (c) E.J. Arlman and P. Cossee, J. Catal., 3 (1964) 99.

7 K.J. Ivin, J.J. Rooney, C.D. Stewart, M.L.H. Green and R. Mahtab, J. Chem. Soc., Chem. Commun., (1978) 604.

8 J.W. Bruno, G.M. Smith, T.J. Marks, C.K. Fair, A.J. Schultz and J.M. Williams, J. Am. Chem. Soc., 108 (1986) 40.

9 (a) K. Tatsumi and A. Nakamura, J. Am. Chem. Soc., 109 (1987) 3195; (b) K. Tatsumi and A. Nakamura, Organometallics, 6 (1987) 427.

10 Z. Dawoodi, M.L.H. Green, V.S.B. Mtetwa, K. Prout, A.J. Schultz, J.M. Williams and T.F. Koetzle, J. Chem. Soc., Dalton Trans., (1986) 1629.

11 Z. Dawoodi, M.L.H. Green, V.S.B. Mtetwa and K. Prout, J. Chem. Soc., Chem. Commun., (1982) 1410.

12 A. Berry, Z. Dawoodi, A.E. Derome, J.M. Dickinson, A.J. Downs, J.C. Green, M.L.H. Green, P.M. Hare, M.P. Payne, D.W.H. Rankin and H.E. Robertson, J. Chem. Soc., Chem. Commun., (1986) 520.

13 M. Mena, M.A. Pellinghelli, P. Royo, R. Serrano and A. Tiripicchio, J. Chem. Soc., Chem. Commun., (1986) 1118.

14 F. Ozawa, J.W. Park, P.B. Mackenzie, W.P. Schaefer, L.M. Henling and R.H. Grubbs, J. Am. Chem. Soc., 111 (1989) 1319.

15 J.Z. Cayias, E.A. Babaian, D.C. Hrncir, S.G. Bott and J.L. Atwood, J. Chem. Soc., Dalton Trans., (1986) 2743.

16 (a) H. Yasuda, T. Arai, T. Okamoto and A. Nakamura, J. Organomet. Chem., 361 (1989) 161; (b) H. Yasuda, H. Yamamoto, T. Arai, A. Nakamura, J. Chen, Y. Kai and N. Kasai, Organometallics, 10 (1991) 4058; (c) H. Yamamoto, Thesis, Osaka University, 1990.

17 H. van der Heijden, A.W. Gal, P. Pasman and A.G. Orpen, Organometallics, 4 (1985) 1847.

18 Z. Dawoodi, M.L.H. Green, V.S.B. Mtetwa and K. Prout, J. Chem. Soc., Chem. Commun., (1982) 802.

19 R.F. Jordan, P.K. Bradley, N.C. Baenziger and R.E. LaPointe, J. Am. Chem. Soc., 112 (1990) 1289.

20 R.M. Bullock, F.R. Lemke and D.J. Szalda, J. Am. Chem. Soc., 112 (1990) 3244.

21 I. Hyla-Kryspin, R. Gleiter, C. Krüger, R. Zwettler and G. Erker, Organometallics, 9 (1990) 517.

22 S.G. Feng, P.S. White and J.L. Templeton, J. Am. Chem. Soc., 112 (1990) 8192.

23 W.P. Piers and J.E. Bercaw, J. Am. Chem. Soc., 112 (1990) 9406.

24 H. Krauledat and H.-H. Brintzinger, Angew. Chem., Int. Ed. Engl., 29 (1990) 1412.

25 A. Nakamura and S. Otsuka, J. Am. Chem. Soc., 94 (1972) 1886.

26 For recent reviews, see: (a) A. Nakamura, J. Organomet. Chem., 400 (1990) 35; (b) A. Nakamura, Coord. Chem. Rev., 109 (1991) 207; (c) H. Yasuda, Y. Kai and A. Nakamura, Adv. Phys. Organomet. Chem., Vol. 2, 1989; (d) H. Yasuda and A. Nakamura, Rev. Chem. Intermediates, 6 (1986) 365.

27 S.A. Cohen, P.R. Auburn and J.E. Bercaw, J. Am. Chem. Soc., 105 (1983) 1136.

28 (a) M.L. Steigerwald and W.A. Goddard, III, J. Am. Chem. Soc., 107 (1985) 5027; (b) A. Stockis and R. Hoffmann, J. Am. Chem. Soc., 102 (1980) 2952; (c) K. Mashima, N. Sakai and H. Takaya, Bull. Chem. Soc. Jpn., 64 (1991) 2475.

29 L.S. Bartell, E.A. Roth, C.D. Hollowell, K. Kuchitzu and J.E. Young, Jr., J. Chem. Phys., 42 (1965) 2683.

30 P. Binger, P. Müller, R. Benn, A. Rufińska, B. Gabor, C. Krüger and P. Betz, Chem. Ber., 112 (1989) 1035.

31 L.J. Guggenberger, P. Meakin and F.N. Tebbe, J. Am. Chem. Soc., 96 (1974) 5420.

32 R.R. Schrock and P.R. Sharp, J. Am. Chem. Soc., 100 (1978) 2389.

33 S.J. McLain, C.D. Wood and R.R. Schrock, J. Am. Chem. Soc., 101 (1979) 4558.

34 J.D. Fellmann, R.R. Schrock and D.D. Traficante, Organometallics, 1 (1982) 481.

35 P.R. Sharp, Organometallics, 3 (1984) 1217.

36 W.J. Evans, T.A. Ulibarri and J.W. Ziller, J. Am. Chem. Soc., 112 (1990) 2314.

37 W.J. Evans, T.A. Ulibarri and J.W. Ziller, J. Am. Chem. Soc., 112 (1990) 219.

38 W.J. Evans, R.A. Keyer, H. Zhang and J.L. Atwood, J. Chem. Soc., Chem. Commun., (1987) 837.

39 C.J. Burns and R.A. Andersen, J. Am. Chem. Soc., 109 (1987) 941.

40 K. Tatsumi and A. Nakamura, unpublished results.

41 H. Yasuda and A. Nakamura, Angew. Chem., Int. Ed. Engl., 26 (1987) 723.

42 (a) Y. Kai, N. Kanehisa, K. Miki, N. Kasai, K. Mashima, K. Nagasuna, H. Yasuda and A. Nakamura, J. Chem. Soc., Chem. Commun., (1982) 191; (b) Crystal data of Cp_2Hf(*s-cis*-1,4-diphenyl-1,3-butadiene) [43]: FW = 554.0 for $C_{26}H_{24}Hf(C_6H_6)_{0.5}$, monoclinic space group $C2/c$, $Z = 8$; $a = 25.762(6)$, $b = 7.842(2)$, $c = 23.946(5)$ Å, $\beta = 111.98(2)°$, U = 4485.8(19) $Å^3$, $d_{calc} = 1.640$, $R = 0.085$ for 3827 reflections.

43 K. Mashima, Thesis, Osaka University, 1985.

44 H. Yasuda and A. Nakamura, unpublished results.

45 T. Okamoto, H. Yasuda, A. Nakamura, Y. Kai, N. Kanehisa and N. Kasai, J. Am. Chem. Soc., 110 (1988) 5008.

46 H. Yamamoto, H. Yasuda, K. Tatsumi, K. Lee, A. Nakamura, J. Chen, Y. Kai and N. Kasai, Organometallics, 8 (1989) 105.

47 K. Mashima, Y. Nakayama and A. Nakamura, unpublished results.

48 G. Jeske, H. Lauke, H. Mauermann, P.N. Swepston, H. Schumann and T.J. Marks, J. Am. Chem. Soc., 107 (1985) 8091.

49 H. Yamamoto, H. Yasuda, K. Yokota, A. Nakamura, Y. Kai and N. Kasai, Chem. Lett., (1988) 1963.

50 H. Yasuda, H. Yamamoto, A. Nakamura and S. Miyake, Polym. Prepr. Jpn., 39 (1990) E788.

51 (a) H. Yasuda, H. Yamamoto, K. Yokota, A. Nakamura and S. Miyake, Polym. Prepr. Jpn., 39 (1990) E734; (b) H. Yasuda, H. Yamamoto, K. Yokota, A. Nakamura and S. Miyake, Polym. Prepr. Jpn., 39 (1990) E735.