

Synthesis, characterization and reactions of ethylene complexes bearing $Ta(\eta^5-C_5R_5)(\eta^4\text{-buta-1,3-diene})$ fragments ($R = H, Me$)[☆]

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Abstract

The ethylene complex $TaCp(\eta^4\text{-butadiene})(\eta^2-C_2H_4)(PMe_3)$ (**2**) was prepared in 77% yield by the reaction of $TaCl_2Cp(\eta^4\text{-butadiene})$ (**1a**) with 2 equiv. of $EtMgI$ in the presence of 1 equiv. of PMe_3 . In the absence of PMe_3 , $TaCp^*(\eta^4\text{-butadiene})(\eta^2-C_2H_4)$ (**3**) was initially formed but this gradually decomposed to give the known metallacyclic compound $Ta(CH_2CH_2CH_2CH_2)Cp^*(\eta^4\text{-butadiene})$ (**4**). Carbonylation of **2** afforded a monocarbonyl complex $TaCp(\text{butadiene})(CO)(PMe_3)$ (**6**) and a dicarbonyl complex $TaCp(\text{butadiene})(CO)_2$ (**7**), while reaction of **2** with diphenylacetylene under UV irradiation gave a reversible addition product $TaCp(\eta^4\text{-butadiene})(\eta^2\text{-PhC}\equiv\text{CPh})(PMe_3)$ (**8**).

Keywords: Tantalum; Ethylene; Carbonylation

1. Introduction

The organometallic chemistry of Group 4 metallocenes has attracted much interest for their importance in the polymerization of α -olefins and the selective carbon-carbon bond forming reactions. Since the ethylene complex of titanocene, $TiCp_2^*(C_2H_4)$ ($Cp^* = \text{pentamethylcyclopentadienyl}$) was prepared by Bercaw et al. [1,2], some 18-electron ethylene complexes of zirconocene [3–6] and hafnocene [7,8] have been reported. Recently ethylene complexes bearing metallocene-like fragments such as $NbCp[N(C_6H_3-2,6-iPr_2)]$ [9], $Mo(NCMe_3)_2$ [10] and $W[N(C_6H_3-2,6-iPr_2)]_2$ [11,12] have been prepared and found to be isoelectronic analogs of MCp_2 where M is a Group 4 metal. In our continuing research into tantalum–diene systems, we found that 14-electron $TaCp(\eta^4\text{-diene})$ fragments are also isoelectronic analogs of Group 4 metallocene fragments and is coordinated by various small molecules [13–17]. Herein we report the preparation and reactions of the tantalum–ethylene complexes.

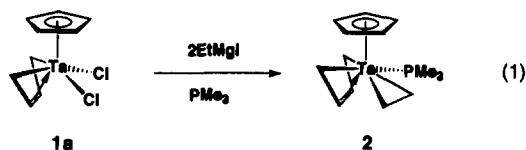
2. Preparation of ethylene complexes of tantalum–butadiene fragments

When the reaction of $TaCl_2Cp(\text{butadiene})$ (**1a**) with 2 equiv. of ethylmagnesium iodide in THF was carried out in the presence of 1 equiv. of PMe_3 , it was possible to isolate ethylene complex **2** as dark brown–purple crystals in 77% yield (eqn. (1)). Complex **2** is highly air- and moisture-sensitive, and a solid sample of **2** decomposed within 2 min upon exposure to air, but **2** is thermally stable on heating at 110°C for several hours. ¹H NMR displayed a doublet at δ 4.36 ($^3J_{HP} = 2.0$ Hz) due to Cp, whose chemical shift is higher by 1.6 ppm than that for **1a**, and a doublet at δ 1.10 ($^2J_{HP} = 7.3$ Hz) due to PMe_3 . We observed six multiplets due to the butadiene ligand and four multiplets around δ 1.0 due to the ethylene moiety, indicating a dissymmetric geometry for **2**. The ¹H–¹H NOESY spectrum confirmed assignments of protons on the butadiene ligand, but four protons due to ethylene could not be fully assigned. In the ¹³C NMR spectrum of **2** ethylene carbons are observed at δ 12.5 and 21.7 with coupling constants $J_{CH} = 149$ and 148 Hz, respectively, which correspond to those (ca. 150 Hz) found for ethylene complexes of early transition metals [1,2,5,10–12,18–22], but these coupling constants are smaller than those of late transi-

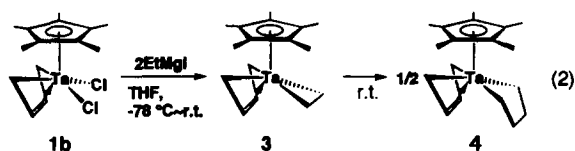
[☆] Dedicated to Professor Dr. Henri Brunner on the occasion of his 60th birthday.

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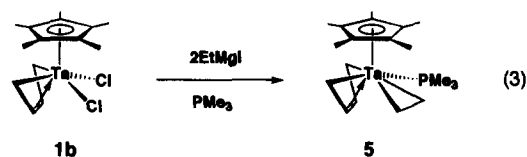
tion metal complexes such as $\text{Os}(\text{C}_2\text{H}_4)(\text{CO})_4$ ($J_{\text{CH}} = 158$ Hz) [23] and $\text{Fe}(\text{C}_2\text{H}_4)(\text{CO})_2[(\text{C}_2\text{F}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_2\text{F}_5)_2]$ (δ 39.9, $J_{\text{CH}} = 160$ Hz) [24]. The former complexes are better represented by a metallacyclopropane structure.



When the reaction product of $\text{TaCl}_2\text{Cp}^*(\text{butadiene})$ (**1b**) with 2 equiv. of EtMgI in THF was monitored by ^1H NMR spectroscopy we observed signals assignable to **3**, i.e. two multiplets at δ 0.10 and 2.52 for ethylene protons attached to the tantalum atom, a singlet at δ 1.77 assignable to the Cp^* protons, and resonances at δ -2.12, 1.13 and 6.39 for the butadiene protons, all in the expected ratios. It is noteworthy that phosphine free ethylene complex of titanium, $\text{TiCp}_2^*(\eta^2\text{-C}_2\text{H}_4)$, may also be prepared by the reaction of $\text{TiCl}_2\text{Cp}_2^*$ with 2 equiv. of EtMgX [25] or by reduction of $\text{TiCl}_2\text{Cp}_2^*$ in a flow of ethylene gas [1,2]. Complex **3** is thermally unstable even at -20°C and gradually decomposes to release ethylene, which further reacts with **3** in the absence of PMe_3 to afford the known metallacyclic compound $\text{Ta}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)\text{Cp}^*(\eta^4\text{-butadiene})$ (**4**) [26] together with unidentified tantalum species; thus all attempts to isolate complex **3** have failed (eqn. (2)). It is relevant here to mention that we recently isolated and characterized crystallographically the phosphine-free benzyne complex $\text{TaCp}^*(\eta^4\text{-butadiene})(\eta^2\text{-C}_6\text{H}_4)$ [27].



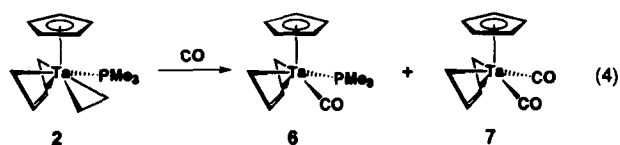
Similarly to that of **2**, the reaction of **1b** with 2 equiv. of EtMgI in the presence of 1 equiv. of PMe_3 gave the corresponding PMe_3 complex **5** (eqn. (3)). The structure of **5** was determined based on its ^1H NMR spectrum. PMe_3 is labile and easily released resulting in the formation of **4** and decomposed tantalum compounds. The large difference in stability between **2** and **5** is attributed to the steric repulsion of the rather bulky Cp^* ligand with PMe_3 . Similar labile coordination of PMe_3 to $\text{TaCp}^*(\eta^4\text{-butadiene})(\eta^2\text{-C}_6\text{H}_4)$ [27] has been observed previously.



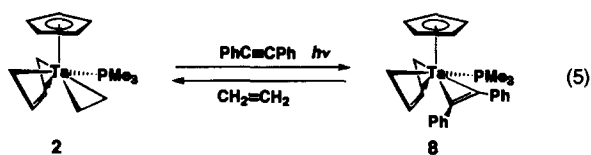
3. Reactions of **2** with carbon monoxide and diphenylacetylene

In contrast to the ethylene complexes of titanocene and zirconocene, coupling reactions of **2** with unsaturated organic substrates did not proceed owing to strong coordination of PMe_3 on tantalum, whereas a Ta(III) complex $\text{TaCp}^*\text{Cl}_2(\text{PMe}_3)_2$ reacted with alkynes or butadiene to give the corresponding $\text{TaCp}^*\text{Cl}_2(\text{L})$ complexes ($\text{L} = \text{alkyne, butadiene}$) and free PMe_3 [28]. However, we observed ligand exchange reactions with carbon monoxide or diphenylacetylene. It is noteworthy that an ethylene complex of vanadium, $\text{VCp}(\eta^2\text{-C}_2\text{H}_4)(\text{PMe}_3)_2$, is reported to show displacement of the ethylene ligand with carbon monoxide or diphenylacetylene giving the corresponding complexes $\text{VCp}(\text{L})(\text{PMe}_3)_2$ ($\text{L} = \text{CO, PhC}\equiv\text{CPh}$) [29].

Complex **2** reacted with carbon monoxide (40 kg cm^{-2}) in 26 h to give a 2:5 mixture of a monocarbonyl complex, $\text{TaCp}(\text{butadiene})(\text{CO})(\text{PMe}_3)$ (**6**), and a dicarbonyl complex, $\text{TaCp}(\text{butadiene})(\text{CO})_2$ (**7**). Further carbonylation (CO 53 kg cm^{-2} ; 78 h) afforded **7** in quantitative yield. A niobium complex similar to **7** has already been reported [30]. The structures of **6** and **7** are supported by their NMR spectral data, as well as IR signals at 1888 cm^{-1} for **6** and 1974 and 1902 cm^{-1} for **7**. These IR data are similar to those found for $\text{MCp}_2(\text{CO})(\text{PMe}_3)$ [31,32] and $\text{MCp}_2(\text{CO})_2$ [33] ($\text{M} = \text{Group 4 metal}$), respectively.



Although the coupling reaction of coordinated ethylene in **2** with alkynes did not proceed, the ligand exchange reaction of the coordinated ethylene with diphenylacetylene occurred under the condition of UV irradiation (eqn. (5)). The reaction was monitored by ^1H NMR spectrum, indicating the formation of **8** together with free ethylene. The structure of **8** is revealed by the comparison of its NMR data with that of the niobium analog [30]. In the dark condition, we observed the reverse reaction, which produced complex **2**.



4. Experimental details

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out by the standard Schlenk technique under argon. All solvents were dried over sodium benzophenone ketyl. A toluene solution of PMe_3 (1.0 M) and diphenylacetylene purchased from Aldrich Chemical Company, Inc. were used as received. Carbon monoxide and ethylene were purchased from Seitetsu Kagaku Co. and were used as received. Complexes $\text{TaCl}_2(\eta^5\text{-C}_5\text{R}_5)(\eta^4\text{-buta-1,3-diene})$ ($\text{R} = \text{H, Me}$) were prepared according to the literature [13,34].

The ^1H (500 MHz, 400 MHz and 270 MHz), ^{13}C (68 MHz) NMR spectra were measured on JEOL JNM-GX500, JEOL JNM-GSX400 or a JEOL JNM-EX270 spectrometers. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded at 109.25 MHz on a JEOL JNM-GSX 270. IR spectra were recorded on a Jasco FT/IR-3 spectrometer with the samples as KBr pellets. Elemental analyses were performed at the Elemental Analysis Center, Faculty of Science, Osaka University. Melting points of all complexes were measured in sealed tubes under argon and are given uncorrected.

4.1. Preparation of $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-buta-1,3-diene})(\eta^2\text{-ethylene})(\text{PMe}_3)$ (**2**)

To a solution of $\text{TaCl}_2(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-buta-1,3-diene})$ (**1a**) (0.578 g, 1.56 mmol) in THF (50 ml) cooled at -78°C were added a solution of PMe_3 (1.03 equiv., 1.60 mmol) in toluene (1.0 M, 1.60 ml) and a solution of EtMgI (2.04 equiv., 3.18 mmol) in ether (0.53 M, 6.00 ml) via syringe. The reaction mixture was stirred for 7 h at 25°C and then left overnight to precipitate magnesium salts. The brown–purple supernatant solution and the solution that was extracted from the residue with hexane (20 ml) were poured into another vessel and evaporated to dryness. Hexane (60 ml) was added to the residue and the solution was stirred at 55°C for 1 h to precipitate the magnesium salts completely. After salts had been separated by centrifugation, the hexane solution was concentrated to 30 ml and kept at -20°C overnight to afford **2** as a dark brown–purple crystals in 77% yield, m.p. 128°C (dec.). Complex **2** is quite air- and moisture-sensitive, but thermally stable; most of the sample of **2** remained undecomposed even when heated in C_6D_6 at 110°C for 6 h. ^1H NMR (270 MHz, C_6D_6 , 303 K): δ -1.08 , -0.45 , -0.43 , 0.93 (4H, m, $=\text{CH}_2$),

0.49 , 0.53 , 0.90 , 1.24 (4H, m, $\text{CH}_2=\text{CH}_2$), 1.10 (9H, d, $^2J_{\text{HP}} = 7.3$ Hz, PMe_3), 4.36 (5H, d, $^3J_{\text{HP}} = 2.0$ Hz, C_5H_5), 4.57 , 5.82 (2H, m, $=\text{CH}-$); ^{13}C NMR (68 MHz, C_6D_6 , 303 K): δ 12.5 (td, $^1J_{\text{CH}} = 149$ Hz, $^2J_{\text{CP}} = 9$ Hz, $\text{CH}_2=\text{CH}_2$), 17.7 (qd, $^1J_{\text{CH}} = 128$ Hz, $^1J_{\text{CP}} = 26$ Hz, PMe_3), 21.7 (t, $^1J_{\text{CH}} = 148$ Hz, $\text{CH}_2=\text{CH}_2$), 27.9 (td, $^1J_{\text{CH}} = 148$ Hz, $^2J_{\text{CP}} = 7$ Hz, $=\text{CH}_2$), 52.0 (td, $^1J_{\text{CH}} = 148$ Hz, $^2J_{\text{CP}} = 9$ Hz, $=\text{CH}_2$), 83.4 (dd, $^1J_{\text{CH}} = 161$ Hz, $^2J_{\text{CP}} = 9$ Hz, $=\text{CH}-$), 90.9 (dd, $^1J_{\text{CH}} = 168$ Hz, $^3J_{\text{CH}} = 9$ Hz, $=\text{CH}-$), 92.6 (dt, $^1J_{\text{CH}} = 175$ Hz, $^2J_{\text{CH}} = 6$ Hz, C_5H_5); $^{31}\text{P}\{^1\text{H}\}$ NMR (109 MHz, C_6D_6 , 303 K): δ -11.4 (PMe_3). Anal. Calc. for $\text{C}_{14}\text{H}_{24}\text{PTa}$: C 41.59; H 5.98%. Found: C 39.60; H 5.64%.

4.2. Preparation of $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\eta^4\text{-buta-1,3-diene})(\eta^2\text{-ethylene})$ (**3**) and $\text{Ta}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\eta^5\text{-C}_5\text{Me}_5)(\eta^4\text{-buta-1,3-diene})$ (**4**)

To a solution of $\text{TaCl}_2(\eta^5\text{-C}_5\text{Me}_5)(\eta^4\text{-buta-1,3-diene})$ (**1b**) (0.421 g, 0.95 mmol) in THF (40 ml) cooled at -78°C were added a solution of EtMgI (2.50 equiv., 2.39 mmol) in ether (0.53 M, 4.50 ml) via syringe. The reaction mixture was stirred for 3 h at 25°C during which time it turned deep green. The solution was then transferred into the other Schlenk tube. Removal of all volatile materials afforded the residue, whose ^1H NMR spectrum exhibits signals of $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\eta^4\text{-buta-1,3-diene})(\eta^2\text{-ethylene})$ (**3**). Complex **3** gradually decomposed to give 0.5 equiv. of $\text{Ta}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\eta^5\text{-C}_5\text{Me}_5)(\eta^4\text{-buta-1,3-diene})$ (**4**) [26] at -20°C ; the color of the solution changed to brown as the reaction proceeded. The instability of **3** seriously inhibited the its isolation. **3**: ^1H NMR (270 MHz, C_6D_6 , 303 K): δ -2.12 (2H, m, $=\text{CH}_2$ anti), 0.10 (2H, m, ethylene), 1.13 (2H, m, $=\text{CH}_2$ syn), 1.77 (15H, s, C_5Me_5), 2.52 (2H, m, ethylene), 6.39 (2H, m, $=\text{CH}-$).

4.3. Preparation of $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\eta^4\text{-buta-1,3-diene})(\eta^2\text{-ethylene})(\text{PMe}_3)$ (**5**)

To a solution of $\text{TaCl}_2(\eta^5\text{-C}_5\text{Me}_5)(\eta^4\text{-buta-1,3-diene})$ (**1b**) (0.582 g, 1.32 mmol) in THF (65 ml) cooled at -78°C were added a solution of PMe_3 (1.05 equiv., 1.38 mmol) in toluene (1.0 M, 1.38 ml) and a solution of EtMgI (2.07 equiv., 2.73 mmol) in ether (0.21 M, 13.00 ml) via syringe. The reaction mixture was stirred for 2 h at 25°C , the color of the solution changed to reddish–brown. Formation of $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\eta^4\text{-buta-1,3-diene})(\eta^2\text{-ethylene})(\text{PMe}_3)$ (**5**) was confirmed by ^1H NMR spectrum, but **5** was not crystallized from the resulting solution because of its high solubility and instability. ^1H NMR (270 MHz, C_6D_6 , 303 K): δ -0.93 , 0.25 , 0.75 (3H, m, $=\text{CH}_2$), -0.09 (2H, m, ethylene), 1.15 (9H, d, $^2J_{\text{HP}} = 6.9$ Hz, PMe_3), 1.31 (2H, m, ethylene), 1.52 (15H, s, C_5Me_5), 3.95 , 5.60 (2H, m,

=CH-). One proton resonance (=CHH) of the butadiene ligand was not assigned because it was overlapped by other peaks.

4.4. Preparation of $Ta(\eta^5-C_5H_5)(\eta^4\text{-buta-1,3-diene})(CO)(PMe_3)$ (**6**) and $Ta(\eta^5-C_5H_5)(\eta^4\text{-buta-1,3-diene})(CO)_2$ (**7**)

A solution of **2** (0.107 g, 0.26 mmol) in toluene (5 ml) was added to a reaction vessel in an autoclave and reacted with pressured CO gas (40 atm) for 26 h at 25°C. The color of the solution changed from brown–purple to yellow–brown. At this time, when the 1H NMR spectrum was measured using a 0.15 ml sample of the solution, $Ta(\eta^5-C_5H_5)(\eta^4\text{-buta-1,3-diene})(CO)(PMe_3)$ (**6**) and $Ta(\eta^5-C_5H_5)(\eta^4\text{-buta-1,3-diene})(CO)_2$ (**7**) were present in the ratio 2:5. After further reaction with CO (53 atm) for 78 h at 25°C, only **7** was obtained from the resulting brown–orange solution. **6**: 1H NMR (270 MHz, C_6D_6 , 303 K): δ -0.53, -0.40, 0.79 (3H, m, =CH₂), 1.11 (9H, d, $^2J_{HP} = 7.6$ Hz, PMe_3), 4.28 (1H, m, =CH-), 4.45 (5H, d, $^3J_{HP} = 1.7$ Hz, C_5H_5), 5.44 (1H, m, =CH-). One proton resonance (=CHH) of the butadiene ligand was not assigned because of its being overlapped by other peaks. IR (KBr cm^{-1}): 1888 (s, CO). **7**: 1H NMR (270 MHz, C_6D_6 , 303 K): δ 0.10 (2H, m, =CH₂ anti), 1.13 (2H, m, =CH₂ syn), 4.40 (5H, s, C_5H_5), 4.69 (2H, m, =CH-); $^{13}C\{^1H\}$ NMR (68 MHz, C_6D_6 , 303 K): δ 36.2 (=CH₂), 74.7 (=CH-), 87.4 (C_5H_5), 228.4 (CO). IR (KBr cm^{-1}): 1902 (s, CO), 1974 (s, CO).

4.5. Preparation of $Ta(\eta^5-C_5H_5)(\eta^4\text{-buta-1,3-diene})(\eta^2\text{-PhC}\equiv\text{CPh})(PMe_3)$ (**8**)

Complex **2** (0.010 g, 0.025 mmol) was dissolved in 0.4 ml of C_6D_6 in a 5-mm NMR tube. To this solution was added one of $PhC\equiv CPh$ (1.09 equiv., 0.027 mmol) in C_6D_6 (0.096 M, 0.28 ml) via syringe at 25°C, and the NMR tube was sealed under reduced pressure. The reaction mixture was subjected to UV radiation for several hours at 25°C, the reaction being monitored by 1H NMR spectroscopy. After irradiation for 9 h, **8** and **2** were detected in the ratio 1.0:1.0. Finally, after irradiation for 56 h, the ratio of **8** to **2** became 3.1:1.0. Further irradiation did not increase the amount of **8**. At this time the color of the solution changed from brown–purple to reddish-brown. When the sample in the NMR tube was analyzed using 1H NMR spectroscopy after having been kept without irradiation for one week, the molar ratio of **2** had increased slightly to 2.6:1.0. **8**: 1H NMR (270 MHz, C_6D_6 , 303 K): δ -0.16, 0.14, 1.27 (3H, m, =CH₂), 1.06 (9H, d, $^2J_{HP} = 7.9$ Hz, PMe_3), 4.89 (5H, d, $^3J_{HP} = 2.0$ Hz, C_5H_5), 5.27, 5.88 (2H, m, =CH-). One proton resonance (=CHH) of the butadiene ligand was not assigned because of being overlapped by other

peaks. $^{31}P\{^1H\}$ NMR (109 MHz, C_6D_6 , 303 K): δ -12.6 (PMe_3).

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References

- [1] S.A. Cohen, P.R. Auburn and J.E. Bercaw, *J. Am. Chem. Soc.*, **105** (1983) 1136.
- [2] S.A. Cohen and J.E. Bercaw, *Organometallics*, **4** (1985) 1006.
- [3] H.G. Alt, C.E. Denner, U. Thewalt and M.D. Rausch, *J. Organomet. Chem.*, **356** (1988) C83.
- [4] H.G. Alt and C.E. Denner, *J. Organomet. Chem.*, **368** (1989) C15.
- [5] P. Binger, P. Müller, R. Benn, A. Rufinska, B. Gabor, C. Krüger and P. Betz, *Chem. Ber.*, **122** (1989) 1035.
- [6] T. Takahashi, M. Murakami, M. Kunishige, M. Saburi, Y. Uchida, K. Kozawa, T. Uchida, D.R. Swanson and E. Negishi, *Chem. Lett.*, (1989) 761.
- [7] S.L. Buchwald, K.A. Kreutzer and R.A. Fisher, *J. Am. Chem. Soc.*, **112** (1990) 4600.
- [8] T. Takahashi, M. Tamura, M. Saburi, Y. Uchida and E. Negishi, *J. Chem. Soc., Chem. Commun.*, (1989) 852.
- [9] A.D. Poole, V.C. Gibson and W. Clegg, *J. Chem. Soc., Chem. Commun.*, (1992) 237.
- [10] P.W. Dyer, V.C. Gibson, J.A.K. Howard, B. Whittle and C. Wilson, *J. Chem. Soc., Chem. Commun.*, (1992) 1666.
- [11] D.S. Williams, M.H. Schofield, J.T. Anhaus and R.R. Schrock, *J. Am. Chem. Soc.*, **112** (1990) 6728.
- [12] D.S. Williams, M.H. Schofield and R.R. Schrock, *Organometallics*, **12** (1993) 4560.
- [13] K. Mashima, Y. Yamanaka, S. Fujikawa, H. Yasuda and A. Nakamura, *J. Organomet. Chem.*, **428** (1992) C5.
- [14] K. Mashima, S. Fujikawa and A. Nakamura, *J. Am. Chem. Soc.*, **115** (1993) 10990.
- [15] K. Mashima, S. Fujikawa, H. Urata, E. Tanaka and A. Nakamura, *J. Chem. Soc., Chem. Commun.*, (1994) 1623.
- [16] K. Mashima, S. Fujikawa, Y. Tanaka, H. Urata, T. Oshiki, E. Tanaka and A. Nakamura, *Organometallics*, **14** (1995) 2633.
- [17] A. Nakamura and K. Mashima, *J. Organomet. Chem.*, **500** (1995) and references cited therein, in press.
- [18] R.R. Schrock and P.R. Sharp, *J. Am. Chem. Soc.*, **100** (1978) 2389.
- [19] S.J. McLain, C.D. Wood and R.R. Schrock, *J. Am. Chem. Soc.*, **101** (1979) 4558.
- [20] L.J. Guggenberger, P. Meakin and F.N. Tebbe, *J. Am. Chem. Soc.*, **96** (1974) 5420.
- [21] J.D. Fellmann, R.R. Schrock and G.A. Rupprecht, *J. Am. Chem. Soc.*, **103** (1981) 5752.
- [22] J.D. Fellmann, R.R. Schrock and D.D. Traficante, *Organometallics*, **1** (1982) 481.
- [23] B.R. Bender, J.R. Norton, M.M. Miller, O.P. Anderson and A.K. Rappé, *Organometallics*, **11** (1992) 3427.
- [24] M. Brookhart, W.A. Chandler, A.C. Pfister, C.C. Santini and P.S. White, *Organometallics*, **11** (1992) 1263.
- [25] K. Mashima, N. Sakai and H. Takaya, *Bull. Chem. Soc. Jpn.*, **64** (1991) 2475.

- [26] J.M. Mayer and J.E. Bercaw, *J. Am. Chem. Soc.*, **104** (1982) 2157.
- [27] K. Mashima, Y. Tanaka and A. Nakamura, unpublished results.
- [28] V.C. Gibson, T.P. Kee and W. Clegg, *J. Chem. Soc., Dalton Trans.*, (1990) 3199.
- [29] B. Hessen, A. Meetsma, F.V. Bolhuis and J.H. Teuben, *Organometallics*, **9** (1990) 1925.
- [30] G.E. Herberich, U. Englert, K. Linn, P. Ross and J. Runsink, *Chem. Ber.*, **124** (1991) 975.
- [31] B. Demerseman, G. Bonquet and M. Bigorgne, *J. Organomet. Chem.*, **132** (1977) 223.
- [32] D.J. Sikora, M.D. Rausch, R.D. Rogers and J.L. Atwood, *J. Am. Chem. Soc.*, **101** (1979) 5079.
- [33] D.J. Sikora, M.D. Rausch, R.D. Rogers and J.L. Atwood, *J. Am. Chem. Soc.*, **103** (1981) 1265.
- [34] H. Yasuda, K. Tatsumi, T. Okamoto, K. Mashima, K. Lee, A. Nakamura, Y. Kai, N. Kanehisa and N. Kasai, *J. Am. Chem. Soc.*, **107** (1985) 2410.