ELSEVIER

Journal of Organometallic Chemistry 627 (2001) 221–225

Journal of Organometallic Chemistry

www.elsevier.nl/locate/jorganchem

Synthesis of *supine–prone* bis(diene)tungsten complexes bearing catecholate and diphenylacetylene ligands

Yuushou Nakayama *[1], Hideo Saito, Norikazu Ueyama, Akira Nakamura *[2]

Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

Received 27 December 2000; received in revised form 16 February 2001; accepted 20 February 2001

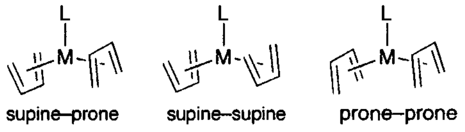
Abstract

Reaction of a mono(catecholato)tetrachlorotungsten(VI) complex, $WCl_4(O_2\text{-}1,2\text{-}C_6H_4)$ (**1a**), with two equivalents of (2,3-dimethyl-2-butene-1,4-diyl)magnesium gave a new class of tungsten bis(diene) complex, $W(O_2C_6H_4)(C_4H_4Me_2)_2$ (**2**), whose *supine–prone* structure was determined by NMR and X-ray analysis. The reaction of **2** with two equivalents of CF_3SO_3H resulted in selective removal of the *prone*-diene ligand to give $W(O_2C_6H_4)(C_4H_4Me_2)(OSO_2CF_3)_2$ (**3**). A similar bis(diene) complex containing diphenylacetylene complex, $W(PhC{\equiv}CPh)(C_4H_4Me_2)_2$ (**4**), was prepared. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Tungsten; 2,3-Dimethylbutadiene; Catecholato; Diphenylacetylene

1. Introduction

Transition metal complexes having conjugated diene ligands are of interest due to their structural diversity and application as catalyst precursor for olefin polymerization and as reagents or intermediates in various organic syntheses [1–5]. Diene complexes are also important because of a wide variety in coordination mode of the diene ligand. For example, geometry of bis(diene) complexes generally presented as $ML(diene)_2$ can formally be classified to three types, *supine–prone*, *supine–supine* and *prone–prone* (Scheme 1) [6]. Among the known bis(diene) complexes, Group 5 metal niobium and tantalum complexes, $MCp(diene)_2$, were confirmed to have *supine–prone* structure [7,8]. Bis(diene) complexes of Group 4 metals, $M(diene)_2(dmpe)$ (M = Ti, Hf; dmpe = bis(dimethylphosphino)ethane), have been found to prefer octahedral geometry [9,10]. In contrast, the reported late transition metal complexes such as $MnL(butadiene)_2$ (L = CO, PR_3) [11,12], $FeL(butadiene)_2$ (L = CO, PR_3) [13,14], $RhCl(butadiene)_2$ [15], and $IrCl(butadiene)_2$ [16] have been shown to have *supine–supine* structure. It is interesting to examine the stereochemistry of bis(diene) complexes of Group 6 metals. However, any $ML(diene)_2$ type complex of Group 6 metals has not been reported.



Scheme 1.

A variety of diene complexes of tungsten prepared until now can be classified into three types; homoleptic tris(diene) complexes, diene carbonyl complexes: $M(CO)_{4-n}(L)_n(\eta^4\text{-diene})$ (M = Cr, Mo, W; L = CO, phosphorus donor ligand) and $M(CO)_2(\eta^4\text{-diene})_2$, and diene derivatives of cyclopentadienyl complexes: $CpMX_nL_m(\eta^4\text{-diene})$ (X = anionic ligand; L = neutral ligand) [17], but other types of tungsten diene complexes have scarcely been explored. Here we report synthesis and characterization of a new class of tungsten bis(diene) complexes bearing catecholate and diphenylacetylene ligands.

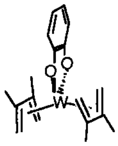
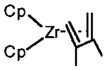
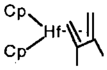
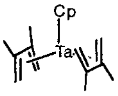
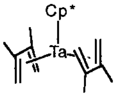
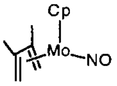
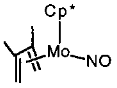
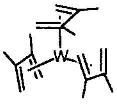
---

[1] *Corresponding author. Present address: Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan. Fax: +81-824-22-7191; e-mail: yushou@hiroshima-u.ac.jp

[2] *Corresponding author. Present address: OM Research, Minami-Ogimachi 7-2-1308, Kita-ku, Osaka 530-0052, Japan.

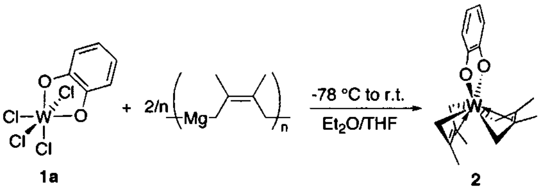
PII: S0022-328X(01)00737-9

Table 1
^{13}C-NMR parameters and sp^n characters of 1,4-carbons in 2,3-dimethylbutadiene complexes of early transition metals. Data from Refs. [7,24–27]

compound	δ	$^1J_{CH}$	n (sp^n character)	ref.
	59.9 45.0	149 148	2.43 2.45	this work
	46.7	143	2.53	[25]
	52.1	132	2.79	[24]
	43.9 43.9	138 140	2.64 2.60	[7]
	53.2 57.6	134 140	2.74 2.60	[7]
	52.2	162	2.16	[26]
	58.2	161	2.18	[26]
	33.5–40.5	148–151	2.36–2.45	[27]

2. Results and discussion

Recently, we reported the first selective synthesis of mono(catecholato)tungsten(VI) complexes, $WCl_4(O_2C_6H_3R\text{-}4)$ (R = H (**1a**), Me (**1b**), Bu^t (**1c**)) [18]. The diene complex, $W(O_2C_6H_4)(C_4H_4Me_2)_2$ (**2**), was obtained from the reaction of **1a** with two equivalents of (2,3-dimethyl-2-butene-1,4-diyl)magnesium in ether as red crystals in 21% yield (Eq. (1)). The complex **2** was air-stable in the solid state. Positive ESI-MS of **2** showed a peak for $(M+H)^+$ at $m/z = 457$.



1a **2** (1)

The ^{1}H-NMR spectrum of **2** was assigned based on ^{1}H-^{1}H COSY and NOESY spectra. The four signals were found assignable to diene 1,4-protons at 2.81 (*supine*), 1.51 (*prone*), 0.79 (*supine*), and 0.10 (*prone*) ppm. Signals of catecholato ligand were observed at 7.45 and 6.98 ppm. If the complex **2** has *supine–supine* or *prone–prone* structure, it would have C_{2v} symmetry to show only two signals of the 1,4-diene protons in the ^{1}H-NMR spectrum. Thus the NMR data indicate that **2** has C_s symmetry suggesting its *supine–prone* structure. ^{13}C-NMR parameters and sp^n characters of 1,4-carbons in 2,3-dimethylbutadiene complexes of early transition metals are summarized in Table 1. Signals for 1,4-carbons of *supine* and *prone* diene ligands in **2** were observed at 59.9 ($^1J_{CH} = 149$ Hz) ppm and 45.0 ($^1J_{CH} = 147$ Hz) ppm, respectively. The extents of sp^n hybridization of 1,4-carbons of *supine* and *prone* diene ligands were calculated by using the Newton's empirical law [19] to be $n = 2.43$ and 2.45, respectively, suggesting that the *prone* diene ligand has slightly higher contribution of $2\sigma-1\pi$ canonical form than the *supine* one. Compared to this tungsten complex, the Groups 4 and 5 metal diene complexes ($n = 2.5 \sim 2.8$) have significantly higher contribution of $2\sigma-1\pi$ canonical form.

The *supine–prone* structure of the bis(diene) complex **2** was confirmed by X-ray crystallography (Fig. 1). Unfortunately, the quality of the data was insufficient to discuss bond distances and angles in detail, but the overall geometry at the metal apparently indicates similarity to the known tris(diene)tungsten where trigonal prism coordination is found.

One of the two diene ligands of the bis(diene) complex **2** has somewhat higher dianionic character as inferred from the protonolysis with two equivalents of

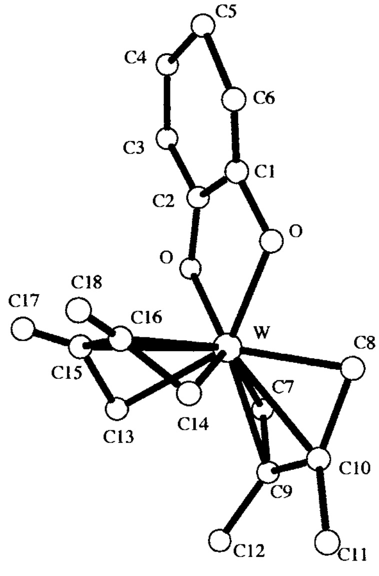


Fig. 1. Molecular structure of $W(O_2C_6H_4)(\eta^4\text{-}2,3\text{-}Me_2C_4H_4)_2$ (**2**).

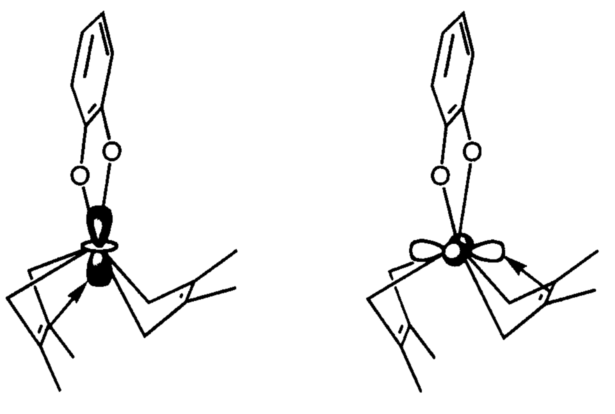
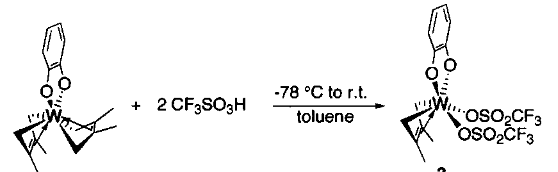


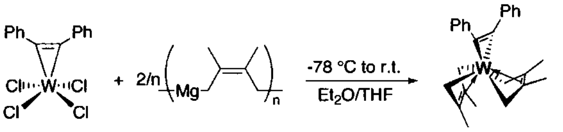
Fig. 2. Schematic drawing of the two important interactions between the frontier orbitals of $W(O_2C_6H_4)(\eta^4\text{-}2,3\text{-}Me_2C_4H_4)_2$ and dimethylbutadiene ligands.

CF_3SO_3H in toluene giving a new mono(diene)bis(triflate) complex, $W(O_2C_6H_4)(C_4H_4Me_2)(OSO_2CF_3)_2$ (**3**) (Eq. (2)). ^{1}H-NMR of **3** showed a set of signals for diene protons at 3.45 (1,4-H), 1.68 (2,3-Me) and 0.85 (1,4-H) ppm. Selective removal of the *prone* diene is thus indicated. This observation suggests that the diene ligand in *prone* fashion is more labile than that in *supine* fashion just like as proposed in the case of the bis(diene) complexes of niobium and tantalum [20]. Similar substitution of one diene ligand by two triflate ligands has been achieved by reactions of diene complexes, $CpTa(1,3\text{-butadiene})_2$ and $Cp_2Zr(1,4\text{-diphenyl-}1,3\text{-butadiene})$ with 1,5-dithioniabicyclo[3.3.0]octane bis(trifluoromethanesulfonate) to give $CpTa(1,3\text{-butadiene})(OSO_2CF_3)_2$ and $Cp_2Zr(OSO_2CF_3)_2$, respectively [21].



2 **3** (2)

We tried the preparation of a similar bis(diene) complex having diphenylacetylene ligand instead of catecholate ligand in **2**. Thus, $W(PhC{\equiv}CPh)Cl_4$ was allowed to react with two equivalents of (2,3-dimethyl-2-butene-1,4-diyl)magnesium to give a bis(diene) complex, $W(PhC{\equiv}CPh)(C_4H_4Me_2)_2$ (**4**). This complex was thermally unstable and gradually decomposed above − 20°C in solution. In ^{1}H-NMR spectrum of **4**, 1,4-protons of *supine* diene were observed at 3.21 and − 0.10 ppm and those of *prone* diene appeared at 1.71 and − 0.64 ppm similarly to those of **2**, indicating that complex **4** has *supine–prone* structure. Resonances of alkyne carbon of **4** at 205 ppm indicate that the alkyne ligand is donating two electrons to the metal center. Thus, the complex **4** can be considered to be a 16-electron complex which is thermally labile even at room temperature. The proton chemical shift values indicate higher electron density at the diene ligand caused by the PhC≡CPh ligand (Eq. (3)).



4 (3)

Assuming the presence of dianionic diene ligands and a d^0 tungsten center, the *supine–prone* geometry of these complexes may be rationalized just like in the case of $LTa(diene)_2$ (L = Cp, Cp*) [7], where the preference is attributed to the favorable electronic structure of two vacant d-orbitals accepting donor orbitals of the two dienes as shown in Fig. 2.

3. Conclusion

A new type of bis(diene) complexes of tungsten was synthesized which have catecholato or diphenylacetylene as ancillary ligands. These complexes were found to have *supine–prone* structure as observed for the known Groups 4 and 5 transition metals. Considering that the bis(diene) complexes of Group 7 manganese or of later metals have *supine–supine* structure, Group 6 metals seem to be the late end of early transition metals in view of the present bonding features with 1,3-diene ligands.

4. Experimental

4.1. General considerations

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out by use of the standard Schlenk technique under an argon atmosphere. $W(O_2C_6H_4)Cl_4$ (**1a**) [18], $W(\eta^2\text{-}PhC{\equiv}CPh)Cl_4$ [22,23], and (2,3-dimethyl-2-butene-1,4-diyl)magnesium [24] were prepared according to the literature. Hexane, THF, toluene, benzene, and ether were purified by distillation under argon after drying over sodium benzophenone ketyl. Dichloromethane was distilled under argon after drying over phosphorus pentoxide. Benzene-d_6 was dried over sodium/potassium alloy and thoroughly degassed by trap-to-trap distillation prior to use.

The ^{1}H- (600, 500, and 400 MHz), and ^{13}C- (150, 125, and 100 MHz) NMR spectra in benzene-d_6, dichloromethane-d_2 were measured on a VARIAN-UNITY-600, a JEOL JNM-LA500, or a JEOL JNM-GSX400 spectrometer. Assignments for ^{1}H- and ^{13}C-NMR peaks for some complexes were aided by 2D

^1H–^1H NOESY, 2D ^1H–^1H COSY, and 2D ^{13}C–^1H COSY spectra. Elemental analysis was performed at the Elemental Analysis Center, Faculty of Science, Osaka University. All melting points of the complexes were measured in sealed tubes under an argon atmosphere and were not corrected. The ESI-MS measurements were performed on a Perkin–Elmer/Sciex API III plus spectrometer.

4.2. $W(O_2C_6H_4)(\eta^4\text{-}2,3\text{-}Me_2C_4H_4)_2$ (2)

A suspension of (2,3-dimethyl-2-butene-1,4-diyl)-magnesium (8.0 ml, 1.4 mmol) in THF was added to a solution of $W(O_2C_6H_4)Cl_4$ (0.29 g, 0.68 mmol) in ether (40ml) at − 78°C. The mixture was allowed to warm to room temperature (r.t.) and stirred for 2 h. Precipitated magnesium salts were removed by centrifugation, and then all volatiles were removed under reduced pressure. The residue was extracted with hot hexane (140 ml) and then with a mixture of hexane (35 ml) and toluene (35 ml). The combined extract was concentrated to 9 ml and the addition of hexane (6 ml) afforded $W(O_2C_6H_4)(\eta^4\text{-}2,3\text{-}Me_2C_4H_4)_2$ (**2**) as red crystals in 21% yield, m.p. 105–108°C. ^1H-NMR (C_6D_6, 30°C, 400 MHz): δ 7.45 (br, 2H, 3,6-$O_2C_6H_4$), 6.98 (br, 2H, 4,5-$O_2C_6H_4$), 2.81 (d, 2H, 1,4-$C_4H_4Me_2$), 1.79 (s, 6H, $C_4H_4Me_2$), 1.51 (d, 2H, 5,8-$C_4H_4Me_2$), 1.48 (s, 6H, $C_4H_4Me_2$), 0.79 (d, 2H, 1′,4′-$C_4H_4Me_2$), − 0.10 (d, 2H, 5′,8′-$C_4H_4Me_2$). ^{13}C-NMR (C_6D_6): δ 119.5 ($O_2C_6H_4$), 118.0 ($O_2C_6H_4$), 113.5 (=CMe–), 110.9 (=CMe–), 69.7 (t, $^1J_{CH} = 149$ Hz, =CH_2), 54.7 (t, $^1J_{CH} = 148$ Hz, =CH_2), 19.8 (=CMe–), 19.4 (=CMe–). Anal. Calc. for $C_{18}H_{24}O_2W$: C, 47.39; H, 5.30. Found: C, 47.89; H, 5.34%. ESI-MS (positive, in MeCN) for ^{184}W m/z 456 (M^+).

4.3. $W(O_2C_6H_4)(\eta^4\text{-}2,3\text{-}Me_2C_4H_4)(OSO_2CF_3)_2$ (3)

To a solution of $W(O_2C_6H_4)(\eta^4\text{-}2,3\text{-}Me_2C_4H_4)_2$ (**2**: 34 mg, 0.07 mmol) in toluene (20 ml) was added a solution of CF_3SO_3H (0.15 mmol) in toluene (1.1 ml) via syringe at − 78°C. The reaction mixture was allowed to warm to ambient temperature and stirred for 1.5 h. The color of the solution changed from red to green, and ^1H-NMR and ESI-MS spectra were measured. ^1H-NMR (C_6D_6, 30°C, 400 MHz): δ 6.86 (m, 2H, 3,6-$C_6H_4O_2$), 6.44 (m, 2H, 4,5-$C_6H_4O_2$), 3.44 (d, 2H, 1,4-$C_4H_4Me_2$), 1.68 (s, 6H, Me), 0.85 (d, 2H, 1′,4′-$C_4H_4Me_2$). ESI-MS (negative, in MeCN) for ^{184}W m/z 713 [$(M + MeCN)^-$].

4.4. $W(\eta^2\text{-}PhC{\equiv}CPh)(\eta^4\text{-}2,3\text{-}Me_2C_4H_4)_2$ (4)

A suspension of (2,3-dimethyl-2-butene-1,4-diyl)-magnesium (0.86 mmol) in THF (5.1 ml) was added to a solution of $W(\eta^2\text{-}PhC{\equiv}CPh)Cl_4$ (0.22 g, 0.43 mmol) in ether (40 ml) at − 78°C. The mixture was allowed to warm to r.t. and stirred for 3 h. Precipitated magnesium salts were removed by centrifugation, and then all volatiles were removed under reduced pressure. The residue was extracted with hexane (105 ml). Concentration and cooling the extract afforded $W(\eta^2\text{-}PhC{\equiv}CPh)(\eta^4\text{-}2,3\text{-}Me_2C_4H_4)_2$ (**4**) as red crystals in 25% yield, m.p. 78°C. ^1H-NMR (C_6D_6, 30°C, 400 MHz): δ 7.77 (d, 4H, o-Ph), 7.30 (t, 4H, m-Ph), 7.08 (t, 2H, p-Ph), 3.21 (d, 2H, $^2J_{HH} = 8.1$ Hz, 1,4-$C_4H_4Me_2$), 2.07 (s, 6H, $C_4H_4Me_2$), 2.06 (s, 6H, $C_4H_4Me_2$), 1.71 (d, 2H, $^2J_{HH} = 5.7$ Hz, 5,8-$C_4H_4Me_2$), − 0.10 (d, 2H, $^2J_{HH} = 8.2$ Hz, 1′,4′-$C_4H_4Me_2$), − 0.64 (d, 2H, $^2J_{HH} = 5.5$ Hz, 5′,8′-$C_4H_4Me_2$). ^{13}C-NMR (C_6D_6): δ 205.2 (CPh), 110.6 (=CMe–), 108.3 (=CMe–), 49.3 (t, =CH_2), 48.4 (t, =CH_2), 22.5 (=CMe–), 21.0 (=CMe–). ESI-MS (positive, in MeCN) for ^{184}W m/z 568 [$(M + MeCN)^+$].

4.5. Crystallographic study of 2

Data were collected on a Rigaku AFC5R diffractmeter using graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å) using an ω–2θ scan mode. The structure was solved by direct methods and refined by full-matrix least-squares on F^2. Unfortunately, most diffractions were significantly broad, and the non-hydrogen atoms could be refined only isotropically.

4.5.1. Crystal and refinement data for 2

$C_{18}H_{24}O_2W$, formula weight = 456.24, monoclinic, space group $P2_1$, $a = 6.981(5)$, $b = 12.245(7)$, $c = 9.850(5)$ Å, $\beta = 107.77(4)°$, $V = 801.9(8)$ Å^3, $Z = 2$, $D_{calc.} = 1.889$ g cm^{-3}, R (R_w) = 0.106 (0.127) for 1382 diffraction data with $I > 3\sigma(I)$ and 85 variables.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 157783 for complex **2**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

Y. N. acknowledges the support by the Grant-in-Aid for Scientific Research on Priority Areas (No. 283, ‘Innovative Synthetic Reactions’) from the Ministry of Education, Science, Sports and Culture, Japan.

References

[1] K. Mashima, A. Nakamura, J. Organomet. Chem. 500 (1995) 261.

[2] A. Nakamura, J. Organomet. Chem. 400 (1990) 35.

[3] H. Yasuda, A. Nakamura, Rev. Chem. Intermed. 6 (1986) 363.

[4] H. Yasuda, K. Tatsumi, A. Nakamura, Acc. Chem. Res. 18 (1985) 120.

[5] G. Erker, C. Krüger, G. Müller, Adv. Organomet. Chem. 24 (1985) 1.

[6] H. Yasuda, A. Nakamura, Angew. Chem. Int. Ed. Engl. 26 (1987) 723.

[7] 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.

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

[9] S.S. Wreford, J.F. Whitney, Inorg. Chem. 20 (1981) 3918.

[10] S.S. Wreford, J. Organomet. Chem. 188 (1980) 353.

[11] G. Huttner, D. Neugebauger, A. Razavi, Angew. Chem. 87 (1975) 353.

[12] R.L. Harlow, P.J. Krusic, R.J. McKinney, S.S. Wreford, Organometallics 1 (1982) 1506.

[13] D.A. Whiting, Cryst. Struct. Commun. 1 (1972) 379.

[14] J.M. McCall, J.R. Morton, Y.L. Page, K.F. Preston, Organometallics 3 (1984) 1299.

[15] A. Immirzi, G. Allegra, Acta Crystallogr. Sect. B 25 (1969) 120.

[16] T.C. van Soest, A. van der Ent, E.C. Royers, Cryst. Struct. Commun. 3 (1973) 527.

[17] M.W. Whiteley, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 5, Elsevier Science, Oxford, 1995, pp. 346–350.

[18] Y. Nakayama, H. Saito, A. Nakamura, Chem. Lett. (1996) 691.

[19] M.D. Newton, J.M. Schulman, M.M. Manus, J. Am. Chem. Soc. 96 (1974) 17.

[20] K. Mashima, S. Fujikawa, Y. Tanaka, H. Urata, T. Oshiki, E. Tanaka, A. Nakamura, Organometallics 14 (1995) 2633.

[21] K. Mashima, T. Oshiki, Y. Matsuo, K. Tani, Chem. Lett. (1997) 793.

[22] A.G.F. Pirinoli, G. Dall'asta, J. Organomet. Chem. 60 (1973) 115.

[23] K.H. Theopold, S.J. Holmes, R.R. Schrock, Angew. Chem. Int. Ed. Engl. 22 (1983) 1010.

[24] H. Yasuda, Y. Kajiwara, K. Mashima, K. Nagasuna, K. Lee, A. Nakamura, Organometallics 1 (1982) 388.

[25] Y. Kai, N. Kanehisa, K. Miki, N. Kasai, M. Akita, H. Yasuda, A. Nakamura, Bull. Chem. Soc. Jpn. 56 (1983) 3735.

[26] N.J. Christensen, A.D. Hunter, P. Legzdins, Organometallics 8 (1989) 930.

[27] P.S. Skell, E.M. Van Dam, M.P. Silvon, J. Am. Chem. Soc. 96 (1974) 626.