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Journal of Organometallic Chemistry 654 (2002) 74–82

Journal of Organometallic Chemistry

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Synthesis of *cis*-dichloride complexes of Group 6 transition metals bearing alkyne and chalcogen-bridged chelating bis(aryloxo) ligands as catalyst precursors for ring-opening metathesis polymerization

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Received 15 January 2002; received in revised form 5 February 2002; accepted 5 March 2002

Abstract

Dichlorotungsten complexes, W(η^2-RC≡CR)(R_2'tbp)Cl_2 (**1**-C_s: R = Ph, R_2'tbp = 2,2′-thiobis(4-methyl-6-*tert*-butylphenoxo) (^{t}Bu$_2$tbp); **2**-C_s: R = Et, R_2'tbp = 2,2′-thiobis(4,6-dimethylphenoxo) (Me$_2$tbp); **3**-C_1: R = Et, R_2'tbp = ^{t}Bu$_2$tbp; **4**-C_1: R = SiMe$_3$, R_2'tbp = ^{t}Bu$_2$tbp), W(η^2-PhC≡CPh)(^{t}Bu$_2$Tebp)Cl_2 (**3**-C_1: ^{t}Bu$_2$Tebp = 2,2′-tellurobis(4-methyl-6-*tert*-butylphenoxo) (**5**-C_1) and Mo(η^2-PhC≡CPh)(^{t}Bu$_2$tbp)Cl_2 (**6**-C_s) were prepared by the reaction of W(η^2-RC≡CR)Cl_4 (R = Ph, Et, SiMe$_3$) with 2,2′-thiobis(4-methyl-6-*tert*-butylphenol), 2,2′-thiobis(4,6-dimethylphenol) or with 2,2′-tellurobis(4-methyl-6-*tert*-butylphenol). The C_s symmetric complex **1**-C_s isomerized to the C_1 isomer **1**-C_1 in solution at room temperature. The molecular structures of **1**-C_1, **3**-C_1, **5**-C_1 and **6**-C_s were determined to reveal their six coordinated *pseudo*-octahedral geometry by X-ray crystallography. The M–C(alkyne) bond distances in the C_s complexes **2**-C_s and **6**-C_s ranging from 2.014(7) to 2.035(6) Å are apparently shorter than those in the corresponding C_1 complexes **1**-C_1, **3**-C_1 and **5**-C_1 ranging from 2.04(1) to 2.09(1) Å. In accordance with the structural data, the resonances of the alkyne carbons of the C_s complexes in ^{13}C-NMR spectra appeared at 233.1–244.5 ppm, typical for four electron donating alkynes, and those of the C_1 complexes appeared at 198.6–215.4 ppm, typical for two electron donating alkynes. The substituent effects of the ligands on the catalytic behavior of the complexes for the ring-opening metathesis polymerization of norbornene derivatives were studied in the presence of Mg(CH_2SiMe_3)$_2$ as a cocatalyst. The catalytic activities of the sulfur-bridged complexes tend to increase with increasing the bulkiness of acetylene ligand. The tellurium-bridged complex **5**-C_1 was found to be remarkably more active than the corresponding sulfur-bridged complexes.

Keywords: Group 6 transition metal complexes; Alkyne ligand; Chalcogen-bridged bis(aryloxo) ligand; Ring-opening metathesis polymerization; Stereo selectivity

1. Introduction

The importance of coordinatively unsaturated alkyne complexes of molybdenum and tungsten has been known since 1963 reported for the zerovalent tris(alkyne) complex [W(CO)(η^2-hex-3-yne)$_3$] [1] and has been highlighted by the extensive review on Mo(II) and W(II) alkyne complexes by Templeton [2]. The alkyne ligands can act as variable electron donors from two to four electron donors in mononuclear molybdenum and tungsten complexes [3], and can be regarded as dianionic π-donors like imido or oxo ligands [4]. Most of the reported Group 6 alkyne complexes have carbonyl and cyclopentadienyl (Cp) type ligands [5], and those without carbonyl and Cp ligands are relatively rare [6].

We recently reported a series of new tungsten dialkyl complexes bearing diphenylacetylene and O–S–O tridentate chelating diaryloxo ligands, W(η^2-PhC≡CPh)(^{t}Bu$_2$tbp)R_2 (^{t}Bu$_2$tbp = 2,2′-thiobis(4-methyl-6-*tert*-butylphenoxo); R = CH_2SiMe_3, CH_2Ph, CH_3), which initiate the ROMP of norbornene to give poly(norbornene) with high molecular weight and high *cis*-content [7]. On the other hand, we also studied the

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PII: S0022-328X(02)01377-3

synthesis and reactivity of titanium complexes having a tellurium bridged chelating diaryloxo ligand, {2,2′-Te(4-Me-6-^{t}BuC$_6$H$_2$O)$_2$} TiX$_2$ (X = Cl, O^{i}Pr) [8]. These complexes catalyzed lower activity in polymerization of ethylene [8] and better living nature in polymerization of ε-caprolactone and L-lactide in comparison with the corresponding sulfur-bridged complexes [9]. This encouraged us to investigate the effect of the bridging atom of the chelating diaryloxo ligand on the ROMP of norbornene by tungsten complexes as well as the alkyl substituent effects of the ligands. Here we report the synthesis and structures of *cis*-dichloride complexes of Group 6 transition metal complexes bearing alkyne and chalcogen-bridged chelating bis(aryloxo) ligands, and their catalytic behavior for the ROMP of norbornene.

2. Results and discussion

2.1. Synthesis and structures of dichlorotungsten complexes **1**-C_s–**6**-C_s

The reaction of W(η^2-RC≡CR)Cl$_4$ (R = Ph, Et, SiMe$_3$) with 2,2′-E(4-Me-6-R′C$_6$H$_2$OH)$_2$ (R′ = ^{t}Bu, Me; E = S, Te) gave dichlorotungsten complexes, W(η^2-RC≡CR)(R$_2'$tbp)Cl$_2$ (**1**-C_s [7], R = Ph, R$_2'$tbp = ^{t}Bu$_2$tbp; **2**-C_s [7], R = Et; R$_2'$tbp = 2,2′-thiobis(4,6-dimethyl-phenoxo) (Me$_2$tbp); **3**-C_1, R = Et; R$_2'$tbp = ^{t}Bu$_2$tbp; **4**-C_1, R = SiMe$_3$; R$_2'$tbp = ^{t}Bu$_2$tbp) and W(η^2-PhC≡CPh)(^{t}Bu$_2$Tebp)Cl$_2$ (**5**-C_1, ^{t}Bu$_2$-Tebp = 2,2′-tellurobis(4-methyl-6-*tert*-butylphenoxo)) as shown in Eqs. (1) and (2). A molybdenum analogue, Mo(η^2-PhC≡CPh)(^{t}Bu$_2$tbp)Cl$_2$ (**6**-C_s), was also prepared according to the literature (Eq. (1)) [7].

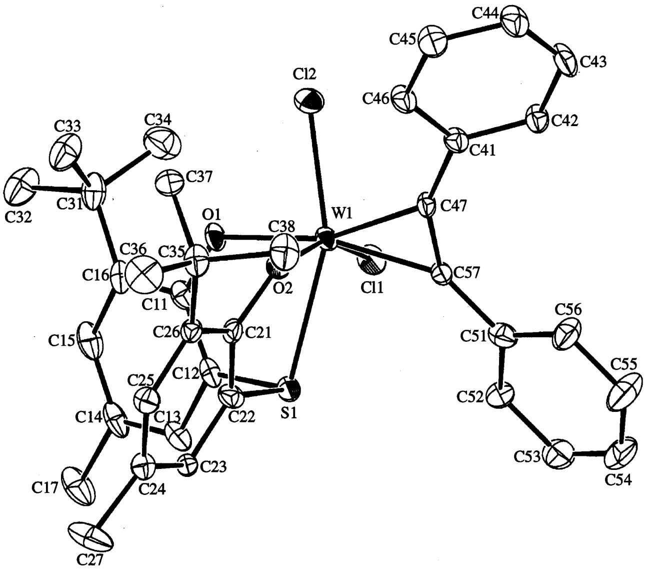
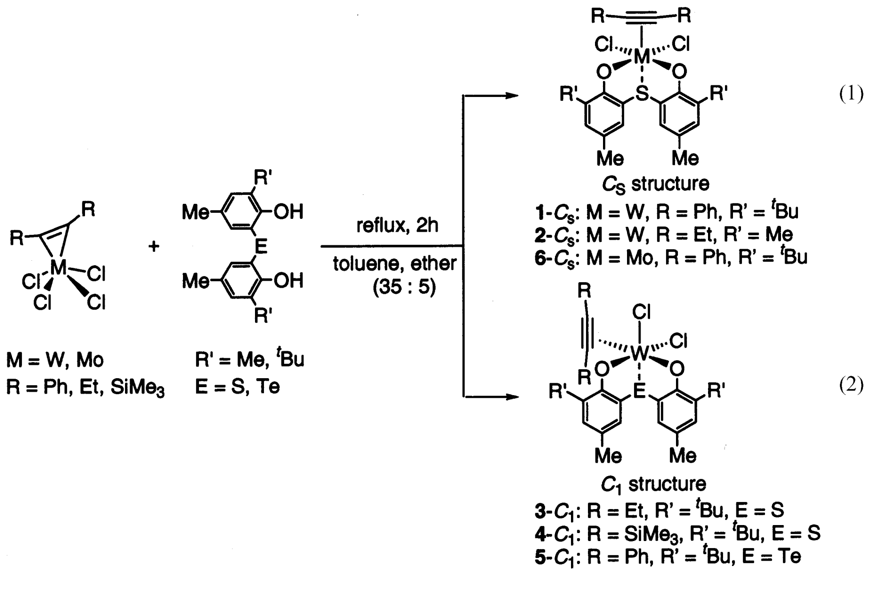


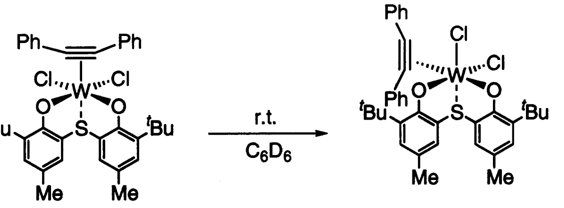
Fig. 1. ORTEP drawing of C_1-W(η^2-PhC≡CPh)(^{t}Bu$_2$tbp)Cl$_2$ (**1**-C_1) with a numbering scheme.

The ^{1}H-NMR spectra of the complexes **1**-C_s, **2**-C_s and **6**-C_s showed one singlet for the protons of the two *tert*-butyl or methyl substituents at 6-position and one singlet for the protons of the two methyl substituents at 4-position, while the aromatic protons at 3- and 5-positions appeared as two doublets. In ^{13}C-NMR spectra of **1**-C_s, **2**-C_s and **6**-C_s, the alkyne carbon resonances appeared as a single peak at 236.5, 244.5 and 233.1 ppm, respectively. The complexes **3**-C_1, **4**-C_1 and **5**-C_1 showed two singlets for the protons of the two *tert*-butyl at 6-position and two singlets for the protons of the two methyl substituents at 4-position, while the aromatic protons at 3- and 5-positions appeared as four



doublets. In the ^{13}C-NMR spectrum, the alkyne carbon resonances were observed as two peaks at 208.5 and 198.6 ppm for **3**-C_1, 202.2 and 190.1 ppm for **4**-C_1, and at 215.4 and 201.8 ppm for **5**-C_1. These data together with the ^{1}H–^{1}H-NOESY, HMQC and HMBC spectra of **1**–**6** suggested that **1**-C_s, **2**-C_s and **6**-C_s had C_s symmetric structure and that **3**-C_1, **4**-C_1 and **5**-C_1 had C_1 symmetric structure, which were also supported by X-ray crystallography of **2**-C_s, **3**-C_1, **5**-C_1 and **6**-C_s (vide infra). The variable temperature ^{1}H-NMR spectra of **3**-C_1 in toluene-d_8 showed the coalescence point for the four methylene alkyne proton resonances at about −20 °C, and an approximate value of $\Delta G^{\ddagger} = 13.2$ kcal mol^{-1} for the alkyne rotation could be estimated.

The C_s complex **1**-C_s gradually isomerized to C_1 complex **1**-C_1 in solution at room temperature (Eq. (3)), which showed two singlets for the protons of the two *tert*-butyl groups at 6-position and two singlets for those of the two methyl substituents at 4-position, and it was also supported by X-ray crystallography of **1**-C_1 (vide infra). We have already reported a similar isomerization of the corresponding bis(trimethylsilylmethyl) complex, W(η^2-PhC≡CPh)(^{t}Bu$_2$tbp)(CH$_2$SiMe$_3$)$_2$, from C_s symmetric structure to C_1 symmetric structure [7]. The least and most sterically crowded complexes, **2**-C_s and **6**-C_s, did not isomerize to C_1 structure under the same conditions. We speculate that the C_s structure of **2** would thermodynamically more stable than C_1 structure, while the C_s structure of **6** might be kinetically stabilized.



1-C_s **1-C_1** (3)

2.2. Molecular structures of dichlorotungsten complexes 1-C_1, 3-C_1, 5-C_1 and 6-C_s by X-ray analysis

Figs. 1–4 show the molecular structures of **1**-C_1, **3**-C_1, **5**-C_1 and **6**-C_s determined by X-ray crystallography, respectively. Selected bond distances and angles of these complexes are summarized in Table 1, which also includes those of the already reported **2**-C_s for comparison [7]. Regarding the alkyne ligands as monodentate ligands, the coordination geometry around the metal center of these complexes can be described as *pseudo*-octahedral. The ^{t}Bu$_2$tbp and Me$_2$tbp ligands coordinate to tungsten in a facial fashion. The complexes **1**-C_1, **3**-C_1 and **5**-C_1 were revealed to have C_1 structure in which the alkyne ligands were at *trans* position to one of the oxygen atom of the chelating diaryloxo ligands. The complex **6**-C_s was revealed to have C_s structure in which the alkyne ligands were at *trans* position to the sulfur atom of the ^{t}Bu$_2$tbp ligand, like the geometry of complex **2**-C_s. The W–S bond distance of the C_1 symmetric 3-hexyne complex **3**-C_1 (2.549(2) Å) is significantly shorter than that of the C_s 3-hexyne complex **2**-C_s (2.638(2) Å) due to the weaker *trans* influence of the chloride ligand than that of the 3-hexyne ligand, and is also shorter than that of the C_1 diphenylacetylene complex **1**-C_1 (2.604(2) Å). The W–Te bond distance (2.828(5) Å) of **5**-C_1 is considerably shorter than the Ti–Te distances in [Ti(^{t}Bu$_2$Tebp)Cl$_2$]$_2$ (2.933(1) Å) [8] and [Ti(^{t}Bu$_2$Tebp)(O^{i}Pr)$_2$]$_2$ (3.021(1) Å)

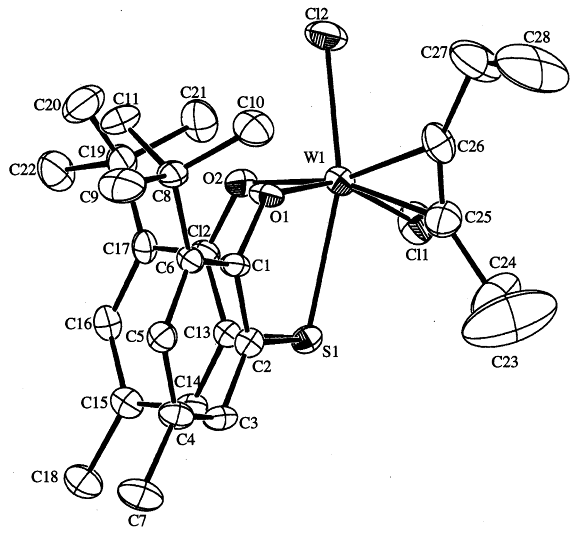


Fig. 2. ORTEP drawing of C_1-W(η^2-EtC≡CEt)(^{t}Bu$_2$tbp)Cl$_2$ (**3**-C_1) with a numbering scheme.

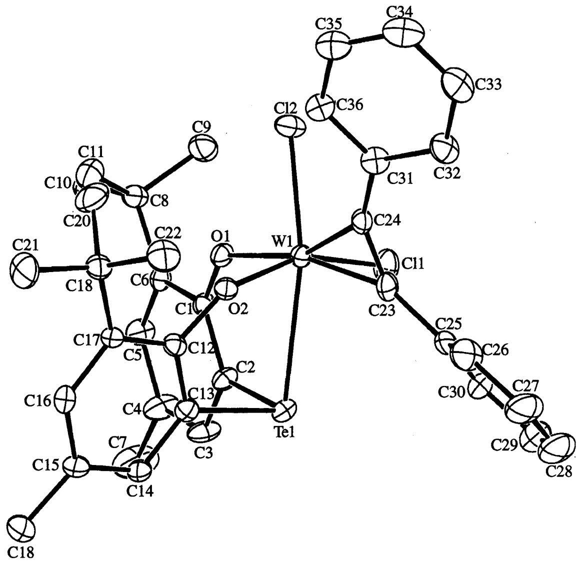


Fig. 3. ORTEP drawing of C_1-W(η^2-PhC≡CPh)(^{t}Bu$_2$Tebp)Cl$_2$ (**5**-C_1) with a numbering scheme.

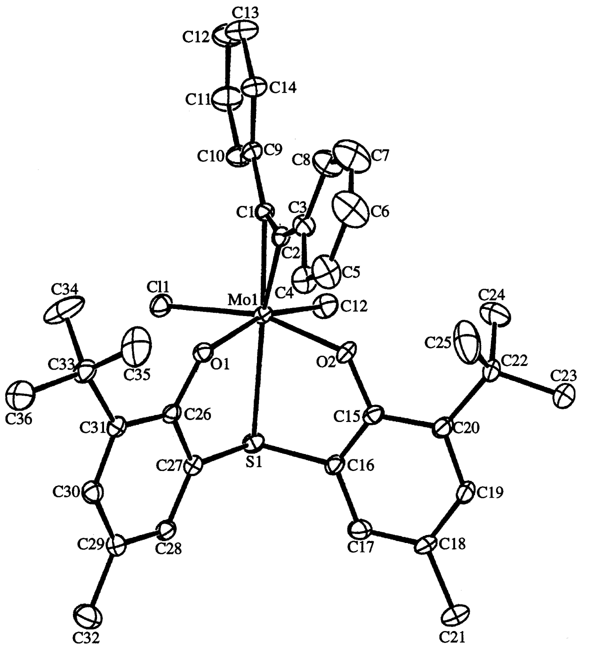


Fig. 4. ORTEP drawing of C_s-Mo(η^2-PhC$\equiv$CPh)(^{t}Bu$_2$tbp)Cl$_2$ (**6**-C_s) with a numbering scheme.

[8] taking into account of similar ionic radii of W^{6+}(0.74 Å) and Ti^{4+}(0.745 Å) [10] due to the stronger coordination of diphenylacetylene ligand. Although the W–Te bond distance of **5**-C_1 is longer than the W–S bond distance of **1**-C_1 (2.604(2) Å) and **3**-C_1 (2.549(2) Å), the W-terminal Cl bond distances *trans* to tellurium in **5**-C_1 (2.350(5) Å) is slightly longer than those of **1**-C_1 (2.325(3) Å) and **3**-C_1 (2.337(3) Å). This suggests that the bridging tellurium atom coordinate to tungsten more strongly than the bridging sulfur atom, as observed in the titanium analogues [8]. This should make the *trans* ligand to tellurium more labile in comparison with those *trans* to sulfur in the sulfur-bridged complexes. The distortion of Cl1–W–Cl2 angle from the octahedral geometry in **3**-C_1 (101.4(1)°) is significantly larger than that in **1**-C_1 (97.56(10)°), **2**-C_s (86.65(7)°) and **5**-C_1 (91.8(1)°), while the O1–W–O2 angle in **5**-C_1 (86.5(3)°) is more deviated from the octahedral geometry than that in **1**-C_1 (88.2(3)°), **2**-C_s (89.4(2)°) and **3**-C_1 (88.7(2)°). The bond distances of the molybdenum complex **6**-C_s are similar to those of the corresponding tungsten complexes, while the O–Mo–O angle of **6**-C_s is considerably wider than the O–W–O angles of the tungsten complexes.

The most notable difference between C_s and C_1 complexes is in the bonding mode of the alkyne ligands. The W–C(alkyne) bond distances in the C_s complex **2**-C_s (2.014(7) Å) are apparently shorter than those in the corresponding C_1 complexes **1**-C_1, **3**-C_1 and **5**-C_1 ranging from 2.04(1) to 2.09(1) Å, indicating that the alkyne ligands in the C_s complex coordinate to tungsten more strongly than those in the C_1 complexes. In accordance with the structural data, the resonances of the alkyne carbons of the C_s complexes **2**-C_s and **6**-C_s appeared at 233.1–244.5 ppm in ^{13}C-NMR spectra, typically for four electron donating alkynes [4]. The ^{13}C-NMR spectra of the C_1 complexes showed signals of the alkyne carbons at 206.7–215.4 ppm, which indicated two electron donating alkynes [4]. Thus, the alkyne ligands in C_s complexes can be considered as four

Table 1
Selected bond distances (Å) and angles (°) of complexes **1**-C_1, **2**-C_s [a], **3**-C_1, **5**-C_1, and **6**-C_s

Complex	**1**-C_1	**2**-C_s [a]	**3**-C_1	**5**-C_1	**6**-C_s
Bond distances					
M–O	2.029(6) (O1)	1.931(5) (O1)	1.878(5) (O1)	2.030(7) (O1)	1.947(4) (O1)
	1.890(7) (O2)	1.945(5) (O2)	2.008(6) (O2)	1.892(7) (O2)	1.947(4) (O2)
M–E (E = S, Te)	2.604(2)	2.638(2)	2.549(2)	2.828(5)	2.613(2)
M–C	2.071(9) (C47)	2.015(8) (C17)	2.04(1) (C25)	2.06(1) (C23)	2.035(6) (C27)
	2.069(9) (C57)	2.014(7) (C18)	2.062(9) (C26)	2.09(1) (C24)	2.011(6) (C28)
M–Cl	2.332(3) (Cl1)	2.350(2) (Cl1)	2.338(2) (Cl1)	2.364(3) (Cl1)	2.385(2) (Cl1)
	2.325(3) (Cl2)	2.394(2) (Cl2)	2.337(3) (Cl2)	2.350(5) (Cl2)	2.378(2) (Cl2)
C≡C(alkyne)	1.301(13)	1.28(1)	1.21(1)	1.31(1)	1.281(8)
Bond angles					
O–M–O	88.2(3)	89.4(2)	88.7(2)	86.5(3)	96.2(2)
C–E–C (E = S, Te)	100.7(4)	102.7(3)	103.0(4)	91.7(4)	107.5(3)
Cl–M–Cl	97.56(10)	86.65(7)	101.4(1)	91.8(1)	88.68(6)
M–O–C	125.9(6) (O1)	130.3(4) (O1)	133.4(5) (O1)	133.1(6) (O1)	128.3(4) (O1)
	132.1(6) (O2)	127.2(4) (O2)	126.2(5) (O2)	138.6(7) (O2)	126.7(4) (O2)
O–M–Cl	85.1(2) (O1)	89.0(1) (O1)	155.9(1) (O1)	85.5(2) (O1)	84.1(1) (O1)
	104.2(2) (O2)	89.0(2) (O2)	84.9(2) (O2)	108.6(2) (O2)	84.6(1) (O2)
C–M–C	36.6(4)	37.1(3)	34.4(4)	36.9(4)	36.9(2)
O–M–E (E = S, Te)	75.3(2)	77.3(2)	76.5(2)	77.0(2)	78.0(1)
	75.9(2)	78.4(1)	79.1(2)	76.6(2)	78.5(1)

[a] Reference [7].

Table 2
ROMP of norbornene by $M(\eta^2\text{-}RC{\equiv}CR)\{E(4\text{-}Me\text{-}6\text{-}R'C_6H_2O)_2\}Cl_2$ ($M = W$, Mo) activated with $Mg(CH_2SiMe_3)_2$

Complex	Yield [a] (%)	$M_n/10^4$ [b]	M_w/M_n [b]	*cis*-Content [c] (%)
1-C_s	5.9	40	2.1	51
2-C_s	< 1			
3-C_1	8.6	31	3.0	59
4-C_1	34	38	2.7 [d]	41
5-C_1	74	69	1.6	24
6-C_s [e]	79	> 200	2.0	54

In toluene, at 60 °C, $[\text{Monomer}]_0/[M] = 100$, $[Mg]/[M] = 1$, Time = 1 h.

[a] Methanol-insoluble fraction.

[b] Determined by GPC analysis in THF calibrated with standard poly(styrene). Theoretical M_n value is less than the experimental one [17].

[c] Microstructure of double bonds in polymer as determined by ^{1}H-NMR spectra [17–19].

[d] Bimodal.

[e] Reference [7].

electron donor ligands, while those in C_1 complexes can be regarded as two electron donor ligands. In the C_1 isomers, the π-donation from the *trans* aryloxo oxygen to the same d-orbital could disturb the donation from the alkyne ligand.

2.3. Polymerization of norbornene by 1-C_s–6-C_s/$Mg(CH_2SiMe_3)_2$

Without cocatalyst, these complexes **1**-C_s–**6**-C_s showed no catalytic activity for the polymerization of norbornene, while the addition of $Mg(CH_2SiMe_3)_2$ to **1**-C_s–**6**-C_s enhanced the activity as summarized in Table 2. In the polymerization of norbornene by the sulfur-bridged complexes **1**-C_s–**4**-C_1/$Mg(CH_2SiMe_3)_2$ systems, the activities of these complexes are in the order of **4** > **3** ≈ **1** ≫ **2**. The use of bulkier alkyne ligands tends to show higher activity. Because we assumed that the isomerization from C_s to C_1 structure should occur before α-H elimination to generate active species [7], the low activity of **2**-C_s could be attributed to its stable C_s structure. The activity of the **1**-C_s/$Mg(CH_2SiMe_3)_2$ system (6% polymer yield in toluene at 60 °C for 1 h) is considerably lower than that of the corresponding bis(trimethylsilylmethyl) complex, $W(\eta^2\text{-}PhC{\equiv}CPh)(^t\text{Bu}_2\text{tbp})(CH_2SiMe_3)_2$ (**7**, 63% polymer yield under the same conditions), and even lower than those of the dibenzyl (22%) and dimethyl (8%) complexes [7]. This might come from the slower generation of active species in the **1**-C_s/$Mg(CH_2SiMe_3)_2$ system. The *cis*-selectivity of the **1**-C_s/$Mg(CH_2SiMe_3)_2$ system (51%) was lower than that of the corresponding dialkyl complex **7** (83%), probably due to some interactions between the active species and the magnesium compounds in the **1**-C_s/$Mg(CH_2SiMe_3)_2$ system.

The tellurium-bridged complex **5** system showed remarkably higher activity than those of the corresponding sulfur-bridged complexes, thus the introduction of W–Te coordination bond is quite effective for enhancing the catalytic activity. The molecular weight of the polymer obtained by **5** is also higher than those obtained by **1**–**4**, thus the higher activity of **5** comes from faster propagation rather than higher concentration of active species. As mentioned above, the tellurium atom coordinates to tungsten more strongly, this should activate the W–C bond *trans* to the tellurium in matallacyclobutane intermediates resulting in the faster propagation in the tellurium-bridged system. Moreover, the C_1 structure of **5** would be more favorable for generation of active species than C_s structure. In contrast to the sulfur-bridged system, the polymer produced by **5** had *trans*-rich structure.

The molybdenum complex (**6**-C_s) showed apparently higher activity than those of the corresponding tungsten complex (**1**-C_s) to give a poly(norbornene) with high molecular weight [7]. Since the molecular structure of **6**-C_s is similar to those of the tungsten derivatives (vide supra), the higher activity of **6**-C_s should result from electronic reasons, possibly higher Lewis acidity of molybdenum.

3. Conclusion

A series of dichlorotungsten complexes of Group 6 metals coordinated with various chelating aryloxo ligands and acetylene ligands, $M(\eta^2\text{-}RC{\equiv}CR)[E(4\text{-}Me\text{-}6\text{-}R'C_6H_2O)_2]Cl_2$ ($M = W$, Mo; R = Ph, Et, $SiMe_3$; $R' = {}^t$Bu, Me; E = S, Te), was synthesized. These complexes had C_s or C_1 structure depending on the metal, bridging atom, and substituents. The $W(\eta^2\text{-}PhC{\equiv}CPh)\{S(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2O)_2\}Cl_2$ (**1**-C_s) isomerized to the C_1 symmetric isomer in solution at ambient temperature. These complexes showed catalytic activity for the ring-opening metathesis polymerization of norbornene upon activation with $Mg(CH_2SiMe_3)_2$. In the polymerization of norbornene by sulfur-containing tungsten complexes, the use of more bulky ligands resulted in the higher polymer yield. The corresponding tellurium-bridged complex (**5**-C_1) showed remarkably higher catalytic activity than those of the corresponding sulfur-bridged complexes.

4. Experimental

4.1. General procedures

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out by the use of standard Schlenk techniques under an argon atmosphere. Diethyl ether, THF, toluene, and *n*-pentane were dried and deoxygenated by distillation over sodium benzophenone ketyl under argon. Benzene-d_6 and toluene-d_8 were distilled from Na–K alloy and thoroughly degassed by trap-to-trap distillation before use. Norbornene (bicyclo[2,2,1]hept-2-ene) purchased from Aldrich Chemical Co. was refluxed over sodium and distilled prior to use. Complexes $\text{M}(\eta^2\text{-RC}\equiv\text{CR})\text{Cl}_4$ [M = W, R = Ph; M = W, R = Et; M = W, R = SiMe$_3$; M = Mo, R = Ph] [11] and 2,2′-tellurois(4-methyl-6-*tert*-butylphenol) [8] were prepared according to the literature. 2,2′-Thiobis(4-methyl-6-*tert*-butylphenol) was supplied by Ciba–Geigy AG.

The ^{1}H- (500, 400 and 270 MHz), and ^{13}C- (125, 100 and 67.5 MHz) NMR spectra in benzene-d_6 and toluene-d_8 were measured on JEOL JNM-LA500, JEOL JNM-GSX400 and JEOL JNM-EX270 spectrometers. Assignments of ^{1}H- and ^{13}C-NMR peaks for some complexes were aided by 2D ^{1}H–^{1}H-NOESY, 2D ^{1}H–^{1}H-COSY, 2D HMQC and 2D HMBC spectra. Elemental analyses were performed at Elemental Analysis Center, Faculty of Science, Osaka University. All melting points (m.p.) of the complexes were measured in sealed tubes under an argon atmosphere. ESIMS measurements were performed on a Perkin–Elmer/Sciex API III plus spectrometer. $\text{W}(\eta^2\text{-PhC}\equiv\text{CPh})[\text{S}(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{O})_2]\text{Cl}_2$ (**1**-C_s), $\text{W}(\eta^2\text{-EtC}\equiv\text{CEt})[\text{S}(4,6\text{-Me}_2\text{C}_6\text{H}_2\text{O})_2]\text{Cl}_2$ (**2**-C_s) and $\text{Mo}(\eta^2\text{-PhC}\equiv\text{CPh})[\text{S}(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{O})_2]\text{Cl}_2$ (**6**-C_s) were prepared according to the literature [7].

4.2. Isomerization of *1* from C_s complex to C_1 complex

Complex **1**-C_s was dissolved in C_6D_6 (0.6 ml) in a 5 mm NMR tube, which was sealed under argon and kept at room temperature (r.t.). The color changed from red to pale orange, and the ^{1}H-NMR spectrum of the solution was measured. The conversion was 42% after 4 days. ^{1}H-NMR (C_6D_6, 30 °C, 270 MHz): δ 8.20 (d, $^4J_{\text{HH}} = 1.35$ Hz, 2H, *o-Ph*C), 7.55 (s, 2H, *o-Ph*C′), 7.30–6.79 (m, 10H, *Ph*C and 3, 5-C_6H_2O), 2.21 (s, 3H, *4-Me*), 1.82(s, 9H, 6-^tBu), 1.77 (s, 3H, 4′-*Me*), 1.27 (s, 9H, 6′-^tBu).

4.3. Preparation of $W(\eta^2\text{-}EtC\equiv CEt)[S(4\text{-}Me\text{-}6\text{-}^tBuC_6H_2O)_2]Cl_2$ (**3**-C_1)

A toluene solution of 2,2′-$\text{S}(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{OH})_2$ (0.40 g, 1.11 mmol) was added to a solution of $\text{W}(\eta^2\text{-EtC}\equiv\text{CEt})\text{Cl}_4$ (0.45 g, 1.11 mmol) in a mixture of toluene (35 ml) and Et_2O (5 ml) at −78 °C. The reaction mixture was stirred for 10 min and then allowed to warm to ambient temperature. The color of the solution changed from red to dark red. After refluxing the solution for 2.5 h, all volatiles were removed under reduced pressure to give microcrystals. Recrystallization from a mixture of THF and *n*-pentane gave $\text{W}(\eta^2\text{-EtC}\equiv\text{CEt})[\text{S}(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{O})_2]\text{Cl}_2$ (**3**-C_1) (0.67 g, 88%) as black crystals, m.p. 185–187 °C. ^{1}H-NMR (Toluene-d_8, −60 °C, 270 MHz): δ 7.17 (d, $^4J_{\text{HH}} = 1.32$ Hz, 1H, 3′-C_6H_2O), 7.15 (d, $^4J_{\text{HH}} = 1.35$ Hz, 1H, 5′-C_6H_2O), 6.82 (d, $^4J_{\text{HH}} = 1.16$ Hz, 1H, 3-C_6H_2O), 6.64 (d, $^4J_{\text{HH}} = 1.32$ Hz, 1H, 5-C_6H_2O), 4.50 (q, $^3J_{\text{HH}} = 9.25$ Hz, 1H, $\text{C}H_2\text{CH}_3$), 4.16 (q, $^3J_{\text{HH}} = 9.41$ Hz, 1H, $\text{C}H_2\text{CH}_3$), 3.72 (q, $^3J_{\text{HH}} = 9.89$ Hz, 1H, $\text{C}H_2\text{CH}_3$), 3.25 (q, $^3J_{\text{HH}} = 9.73$ Hz, 1H, $\text{C}H_2\text{CH}_3$), 2.19 (s, 3H, 4-*Me′*), 1.78 (s, 9H, 6-^tBu), 1.69 (s, 3H, 4-*Me*), 1.32 (t, $^3J_{\text{HH}} = 7.50$ Hz, 6H, $\text{CH}_2\text{C}H_3$), 1.13 (t, $^3J_{\text{HH}} = 7.25$ Hz, 6H, $\text{CH}_2\text{C}H_3$), 1.09 (s, 9H, 6-^tBu). ^{13}C-NMR (Toluene-d_8, −60 °C, 67.5 MHz): 208.5 (*C′*Et), 198.6 (*C*Et), 165.7 (1′-$C_6\text{H}_2\text{O}$), 161.3 (1-$C_6\text{H}_2\text{O}$), 142.6 (6′-$C_6\text{H}_2\text{O}$), 139.0 (6-$C_6\text{H}_2\text{O}$), 133.9 (4′-$C_6\text{H}_2\text{O}$), 130.5 (5′-$C_6\text{H}_2\text{O}$), 130.1 (4-$C_6\text{H}_2\text{O}$), 129.2 (5-$C_6\text{H}_2\text{O}$), 128.4 (3′-$C_6\text{H}_2\text{O}$), 127.6 (3-$C_6\text{H}_2\text{O}$), 124.6 (2′-$C_6\text{H}_2\text{O}$), 120.0 (2-$C_6\text{H}_2\text{O}$), 36.8 ($C\text{H}_2\text{CH}_3$), 36.0 (6-$C'\text{Me}_3$), 35.0 (6-$C\text{Me}_3$), 29.8 (6-$\text{C}Me'_3$), 29.2 (6-$\text{C}Me_3$), 21.2 (4-*Me′*), 20.50(4-*Me*), 16.4 ($\text{CH}_2C'\text{H}_3$), 16.3 (CH_2CH_3). Anal. Calc. for $\text{C}_{28}\text{H}_{38}\text{Cl}_2\text{O}_2\text{SW}$: C, 48.50; H, 5.52. Found: C, 48.80; H, 5.49%.

4.4. Preparation of $W(\eta^2\text{-}Me_3SiC\equiv CSiMe_3)[S(4\text{-}Me\text{-}6\text{-}^tBuC_6H_2O)_2]Cl_2$ (**4**-C_1)

A toluene solution of 2,2′-$\text{S}(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{OH})_2$ (0.26 g, 0.72 mmol) was added to a solution of $\text{W}(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)\text{Cl}_4$ (0.36 g, 0.72 mmol) in a mixture of toluene (35 ml) and Et_2O (5 ml) at −78 °C. The reaction mixture was stirred for 10 min and then allowed to warm to ambient temperature. The color of the solution changed from red to dark red. After refluxing the solution for 2 h, all volatiles were removed under reduced pressure. Recrystallization from a mixture of toluene and *n*-pentane gave $\text{W}(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)[\text{S}(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{O})_2]\text{Cl}_2$ (**4**-C_1) (0.29 g, 44%) as black crystals. ^{1}H-NMR (C_6D_6, 30 °C, 500 MHz): δ 7.30 (s, $^4J_{\text{HH}} = 1.51$ Hz, 1H, 3′-C_6H_2O), 7.20 (s, 1H, 5′-C_6H_2O), 7.04 (s, $^4J_{\text{HH}} = 1.10$ Hz, 1H, 3-C_6H_2O), 6.71 (s, $^4J_{\text{HH}} = 1.53$ Hz, 1H, 5-C_6H_2O), 2.21 (s, 3H, 4′-*Me*), 1.80 (s, 3H, 4-*Me*), 1.75 (s, 9H, 6′-^tBu), 1.03 (s, 9H, 6-^tBu), 0.75 (s, 9H, $\text{Si}Me'_3$), 0.43 (s, 9H, $\text{Si}Me_3$). ^{13}C-NMR (C_6D_6, 30 °C, 125 MHz): 202.2 (MeSi*C*), 190.1 (MeSi*C′*), 165.7 (1′-$C_6\text{H}_2\text{O}$), 161.4 (1-$C_6\text{H}_2\text{O}$), 143.0 (6′-$C_6\text{H}_2\text{O}$), 139.7 (6-$C_6\text{H}_2\text{O}$), 130.9 (5′-$C_6\text{H}_2\text{O}$), 130.2 (5-$C_6\text{H}_2\text{O}$), 134.5 (4′-$C_6\text{H}_2\text{O}$), 131.6 (4-$C_6\text{H}_2\text{O}$), 128.6 (3′-$C_6\text{H}_2\text{O}$), 127.8 (3-$C_6\text{H}_2\text{O}$), 35.7 (6′-$C\text{Me}_3$), 34.4 (6-$C\text{Me}_3$), 29.9 (6′-$\text{C}Me_3$), 29.3 (6-$\text{C}Me_3$), 20.8 (4′-*Me*), 20.7 (4-*Me*), 2.79 ($\text{Si}Me_3$), 1.8 ($\text{Si}Me'_3$). Anal. Calc. for $\text{C}_{30}\text{H}_{48}\text{Cl}_2\text{O}_2\text{S}_1\text{Si}_2\text{W}_1\cdot0.5\text{C}_5\text{H}_{12}$: C, 47.74; H, 6.41. Found: C, 47.62; H, 6.39%. ESIMS for m/z: 835 $[\text{M}]^-$.

4.5. Preparation of $W(\eta^2\text{-}PhC{\equiv}CPh)[Te(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2O)_2]Cl_2$ (**5**-C_1)

A toluene solution of 2,2′-Te(4-Me-6-^{t}Bu$C_6H_2OH)_2$ (0.39 g, 0.87 mmol) was added to a solution of W(η^2-PhC≡CPh)Cl_4 (0.43 g, 0.87 mmol) in a mixture of toluene (35 ml) and Et_2O (5 ml) at −78 °C. The reaction mixture was stirred for 10 min and then allowed to warm to ambient temperature. The color of the solution changed from red to dark red. After refluxing the solution for 2 h, all volatilies were removed under reduced pressure. Recrystallization from a mixture of toluene and *n*-pentane gave W(η^2-PhC≡CPh)[Te(4-Me-6-^{t}Bu$C_6H_2O)_2]Cl_2$ (**5**) (0.58 g, 76%) as black crystals. ^{1}H-NMR (C_6D_6, 30 °C, 500 MHz): δ 8.15 (d, 2H, *o-Ph*C), 7.51 (d, 2H, *o-Ph′*C), 7.29 (t, 2H, *m-Ph*C), 7.20 (s, ${}^4J_{HH} = 2.1$ Hz, 1H, 3′-C_6H_2O), 7.19 (s, ${}^4J_{HH} = 2.1$ Hz, 1H, 5′-C_6H_2O), 7.14 (t, 2H, *m-Ph′*C), 6.79 (s, ${}^4J_{HH} = 1.37$ Hz, 1H, 3-C_6H_2O), 6.74 (s, ${}^4J_{HH} = 1.83$ Hz, 1H, 5-C_6H_2O), 7.08 (d, 1H, *p-Ph*C), 6.94 (d, 1H, *p-Ph′*C), 3.62 (m, 2H, *THF*), 2.16 (s, 3H, 4′-*Me*), 1.78 (s, 9H, 6′-^{t}*Bu*), 1.72 (s, 3H, 4-*Me*), 1.46 (m, 2H, *THF*), 1.23 (s, 9H, 6-^{t}*Bu*). ^{13}C-NMR (C_6D_6, 30 °C, 125 MHz): 215.4 (Ph*C*), 201.8 (Ph*C′*), 170.9 (1′-C_6H_2O), 166.2 (1-C_6H_2O), 147.5 (1′-*Ph*C), 143.9 (6′-C_6H_2O), 140.7 (6-C_6H_2O), 138.7 (1-*Ph*C), 134.5 (5-C_6H_2O), 134.3 (4′-C_6H_2O), 133.9 (2-*Ph*C), 133.5 (5′-C_6H_2O), 131.1 (4-*Ph*C), 131.1 (4-C_6H_2O), 130.9 (3′-C_6H_2O), 130.3 (4′-*Ph*C), 130.0 (3-C_6H_2O), 129.1 (3′-*Ph*C), 128.9 (3-*Ph*C), 128.8 (2′-*Ph*C), 116.3 (2-C_6H_2O), 111.9 (2-C_6H_2O), 67.8 (*THF*), 35.9 (6′-*C*Me_3), 35.3 (6-*C*Me_3), 30.0 (6′-C*Me*$_3$), 29.8 (6-C*Me*$_3$), 25.8 (*THF*), 20.7 (4′-*Me*), 20.5 (4-*Me*). Anal. Calc. for $C_{36}H_{38}Cl_2O_2TeW \cdot 0.5C_4H_8O$: C, 49.55; H, 4.60. Found: C, 49.79; H, 4.58%. ESIMS for *m/z*: 884 [M]$^-$.

4.6. Polymerization of norbornene

A solution of $Mg(CH_2SiMe_3)_2$ (0.01 mmol) in toluene (50 μl) was added to a solution of W(η^2-PhC≡CPh)[S(4-Me-6-^{t}Bu$C_6H_2O)_2]Cl_2$ (**1**-C_s) (0.01 mmol) in toluene (0.75 ml) at −78 °C. The reaction mixture was stirred for 10 min and then allowed to be stirred at ambient temperature for 15 min, followed by cooling to −78 °C. To this solution of **1**-C_s–$Mg(CH_2SiMe_3)_2$ in toluene was added a solution of norbornene (100 equivalents, 1 mmol) in toluene (0.2 ml) at −78 °C. The reaction mixture was stirred for 5 min and then allowed to be stirred at 60 °C for 1 h. A large excess of MeOH was added to the resulting reddish viscous solution to precipitate a white polymer. The polymer was washed with MeOH and then dried in vacuo. ^{1}H-NMR ($CDCl_3$, 30 °C, 270 MHz): δ 5.39(br), 2.95(br), 2.09(br), 1.92(br), 1.49(br), 1.21 (q(br)).

4.7. GPC analysis of the polymers

GPC analyses were carried out using Tosoh TSKgel HXL-H and -L columns connected to a Tosoh RI-8012 detector. Samples were prepared in THF (0.1–0.3% (w/v)) and were filtered through an Advantec DISMIC-25JP filter in order to remove particulate before injection. GPC columns were calibrated versus commercially available polystyrene standards (Polymer Laboratories Ltd.) whose molecular weight ranged from 500 to 2.15×10^6.

4.8. Crystallographic data collections and structure determination of **1**-C_1, **3**-C_1, **5**-C_1 and **6**-C_s

A crystal of **1**-C_1 suitable for X-ray diffraction studies was mounted on a cryoloop. The measurement of **1**-C_1 was made on a Rigaku R-AXIS-RAPID imaging plate diffractometer with graphite monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71069$). Relevant crystal and data statistiC_s are summarized in Table 3. Indexing was performed from one oscillations, which were exposed for 5.0 min. The camera radius was 127.40 mm. Readout was performed in the 0.100 mm pixel mode. A symmetry-related absorption correction using the program ABSCOR was applied [12]. The data was corrected for Lorentz and polarization effects. The structures of complex **1**-C_1 was solved by direct methods (SIR-92) [13], expanded using Fourier techniques (DIRDIF 94) [14], and refined by full-matrix least-squares refinement (SHELXL-97) [15]. In the subsequent refinement the function $\Sigma\omega(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factors amplitudes, respectively. The agreement indices are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma\omega(F_o^2 - F_c^2)^2/\Sigma\omega(F_o^2)^2]^{1/2}$. The positions of all non-hydrogen atoms for the complexes were found from a difference Fourier electron density maps and refined anisotoropically. All hydrogen atoms were placed in calculated positions (C–H = 0.95 Å) and kept fixed.

The X-ray diffraction studies were carried out in sealed glass capillaries under an argon atmosphere. The crystals of complexes **3**-C_1, **5**-C_1 and **6**-C_s were mounted on Rigaku AFC-7R or AFC-5R four-circle diffractometers for data collection using Mo–K$_\alpha$ (graphite monochromated, $\lambda = 0.71069$) radiation. Relevant crystal and data statistics are summarized in Table 3. The unit cell parameters and the orientation matrix at 23 °C were determined by a least-squares fit to 2θ values of 25 strong higher reflections for these complexes. Three standard reflections were chosen and monitored every 150 reflections. Empirical absorption correction was carried out on the basis of an azimuthal scan. Complexes **3**-C_1, **5**-C_1 and **6**-C_s showed no significant intensity decay during the data collection. The structures of the complexes **3**-C_1, **5**-C_1 and **6**-C_s were solved by

Table 3
Crystal data and collection parameters for **1**-C_1, **3**-C_1, **5**-C_1 and **6**-C_s

Complex	**1**-C_1	**3**-C_1	**5**-C_1	**6**-C_s
Formula	$C_{36}H_{38}Cl_2O_2SW$	$C_{28}H_{38}Cl_2O_2SW$	$C_{38}H_{42}Cl_2O_2WTe$	$C_{43}H_{46}Cl_2O_2SMo$
Formula weight	789.47	693.42	921.10	793.74
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (#14)	$P2_1/a$ (#14)	$P2_1/a$ (#14)	$P2_1/c$ (#14)
a (Å)	10.2438(5)	16.090(4)	17.54(3)	20.014(5)
b (Å)	17.1335(8)	11.113(5)	18.706(9)	11.021(8)
c (Å)	19.3165(13)	17.029(3)	12.09(2)	20.518(6)
α (°)				
β (°)	96.031(2)	97.79(2)	104.5(1)	115.37(2)
γ (°)				
V (Å^3)	3371.5(3)	3016(1)	3841(9)	4089(3)
Z	4	4	4	4
D_{calc} (g cm^{-3})	1.555	1.527	1.592	1.289
$F(000)$	1576.00	1384.00	1800.00	1648.00
μ [Mo–K$_\alpha$] (cm^{-1})	36.77	41.01	39.24	5.35
Temperature (K)	193 (1)	296 (1)	296 (1)	296 (1)
Scan speed (° min^{-1})		16.0	16.0	16.0
Scan width (°)		1.42+0.35tan θ	1.00+0.3tan θ	1.68+0.35tan θ
$2\theta_{max}$ (°)		55.0	54.9	55.0
Unique data (R_{int})	7512 (0.0809)	6936 (0.047)	8793 (0.038)	9403 (0.105)
Number of observations	5708	3447	3488	4449
Number of variables	387	307	403	442
R	0.0778	0.040	0.052	0.047
R_w	0.1654 (all data)	0.044	0.057	0.050
Goodness-of-fit	1.409	1.23	1.20	1.66

direct methods (SHELXS-86) [16], expanded using Fourier techniques (DIRDIF 94) [14], and refined by the full-matrix least-square method. Measured non-equivalent reflections with $I > 2.0\sigma(I)$ were used for the structure determination for **3**-C_1 and **5**-C_1. For **6**-C_s measured non-equivalent reflections with $I > 3.0\sigma(I)$ were used. In the subsequent refinement the function $\Sigma\omega(|F_o|-|F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factors amplitudes, respectively. The agreement indices are defined as $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R_w=[\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega(|F_o|)^2]^{1/2}$ where $\omega^{-1}=\sigma^2(F_o)=[\sigma_c^2(F_o)+p^2/4(F_o^2)]$. The positions of all non-hydrogen atoms for these complexes were found from a difference Fourier electron density map and refined anisotropically. Hydrogen atoms were placed in calculated positions (C–H = 0.95 Å) and constrained to ride on their respective carbon atoms.

All calculations were performed using the TEXSAN crystallographic software package, and illustrations were drawn with ORTEP.

5. Supplementary material

Crystallographic data for the structural analysis of **1**-C_1, **3**-C_1, **5**-C_1 and **6**-C_s have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 174243, 174195, 174244 and 174242, respectively. 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).

References

[1] D.P. Tate, J.M. Augal, J. Am. Chem. Soc. 85 (1963) 2174.

[2] J.L. Templeton, Adv. Organomet. Chem. 29 (1989) 1.

[3] (a) R.B. King, Inorg. Chem. 7 (1968) 1044;
(b) J.W. McDonald, J.L. Corbin, W.E. Newton, J. Am. Chem. Soc. 97 (1975) 1970;
(c) J.W. McDonald, W.E. Newton, C.T. Creedy, J. Organomet. Chem. 92 (1975) C25;
(d) J.L. Templeton, B.C. Ward, J. Am. Chem. Soc. 102 (1980) 3261.

[4] S. Otsuka, A. Nakamura, Adv. Organomet. Chem. 9 (1990) 328.

[5] (a) R.M. Laine, R.E. Moriarty, R. Bau, J. Am. Chem. Soc. 94 (1972) 1402;
(b) B. Capelle, A.L. Beauchamp, M. Dartiguenave, Y. Dartiguenave, J. Chem. Soc. Chem. Commun. (1982) 566;
(c) F.R. Kreissl, W.J. Sieber, P. Hofmann, J. Riede, M. Wolfgruber, Organometallics 4 (1985) 788;
(d) A. Mayr, K.S. Lee, M.A. Kjelsberg, D.V. Engen, J. Am. Chem. Soc. 108 (1986) 6079;
(e) W.A. Nugent, J.M. Mayer, Metal–Ligand Multiple Bonds, vol. 1, Wiley-Interscience, New York, 1987, p. 7;
(f) A. Mayr, A.M. Dorries, A.L. Rheingold, S.J. Geib, Organometallics 9 (1990) 964;
(g) P.K. Baker, K.R. Flower, M.G.B. Drew, Organometallics 12 (1993) 276;
(h) N. Prem, in: E.W. Abel, E.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic. Chemistry II, vol. 5, Elsevier,

Oxford, 1995, p. P363;
(i) W.-Y. Yeh, C.-S. Ting, S.-M. Chien, S.-M. Peng, G.-H. Lee, Inorg. Chim. Acta 255 (1997) 335;
(j) S.M. Waterman, M.G. Humphrey, V.-A. Tolhurst, M.I. Bruce, P.J. Low, D.C.R. Hockless, Organometallics 17 (1998) 5789;
(k) H. Adams, M.T. Atkinson, M.J. Morris, J. Organomet. Chem. 580 (1999) 265.

[6] (a) C.E. Kriley, J.L. Kerschner, P.E. Fanwick, I.P. Rothwell, Organometallics 12 (1993) 2051;
(b) T.E. Baroni, J.A. Heppert, R.R. Hodel, R.P. Kingsborough, M.D. Morton, A.L. Rheigold, G.P.A. Yap, Organometallics 15 (1996) 4872;
(c) P.K. Baker, M.G.B. Drew, M.M. Meehan, J. Szewczyk, J. Organomet. Chem. 580 (1999) 265;
(d) T.W. Crane, P.S. White, J.L. Templeton, Organometallics 18 (1999) 1897;
(e) N. Aimeloglou, P.K. Baker, M.G.B. Drew, B. Glaeser, F. Holland, M.M. Meehan, J. Organomet. Chem. 604 (2000) 191;
(f) T.W. Crane, P.S. White, J.L. Templeton, Inorg. Chem. 39 (2000) 1081;
(g) G. Guillemot, E. Solari, C. Floriani, N. Re, C. Rizzoli, Organometallics 19 (2000) 5218.

[7] Y. Nakayama, H. Saito, N. Ueyama, A. Nakamura, Organometallics 18 (1999) 3149.

[8] Y. Nakayama, K. Watanabe, N. Ueyama, A. Nakamura, A. Harada, J. Okuda, Organometallics 19 (2000) 2498.

[9] Y. Takashima, Y. Nakayama, K. Watanabe, T. Itono, N. Ueyama, A. Nakamura, A. Harada, J. Okuda, manuscript in press.

[10] R.D. Shannon, Acta Crystallogr. Sect. A 32 (1976) 751.

[11] (a) E. Hey, F. Weller, K. Dehnicke, Z. Anorg. Allg. Chem. 514 (1984) 25;
(b) K.H. Theopold, S.J. Holmes, R.R. Schrock, Angew. Chem. Int. Ed. Engl. 22 (1983) 1010;
(c) E. Hey, F. Weller, K. Dehnicke, Z. Anorg. Allg. Chem. 514 (1984) 18.

[12] T. Higashi, Program for Absorption Correction, Rigaku Corporation, Tokyo, Japan, 1995.

[13] A. Altomare, M.C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidori, J. Appl. Crystallogr. 27 (1994) 435.

[14] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder, R. Israel, J.M.M. Smits, The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegan, The Netherlands, 1994.

[15] G.M. Sheldrick, Program for the solution of Crystal structures, Universität Göttingen, Germany, 1997.

[16] G.M. Sheldrick, in: G.M. Sheldrick, C. Krüger, R. Goddard (Eds.), Crystallographic Computing, vol. 3, Oxford University Press, Oxford, 1985.

[17] L.R. Gilliom, R.H. Grubbs, J. Am. Chem. Soc. 108 (1986) 733.

[18] N.A. Petasis, D.-K. Fu, J. Am. Chem. Soc. 115 (1993) 7208.

[19] J.G. Hamilton, K.J. Ivin, J.J. Rooney, J. Mol. Catal. 28 (1985) 255.