Synthesis and Characterization of Mononuclear Titanium Complexes Containing a Bis(phenoxy) Ligand Derived from 2,2′-Methylene-bis(6-*tert*-butyl-4-methylphenol)

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A series of new titanium complexes of the general type Ti(mbmp)X_2 (X = Br, I; OMe, O*i*Pr, O*t*Bu), containing a bidentate bis(phenoxy) ligand derived from 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) (mbmpH_2), was prepared. The ^{1}H-chemical shifts for the protons of the methylene link were found to vary considerably as a function of the ligand X. Reaction of Ti(O*i*Pr)$_4$ with two equivalents of mbmpH_2 gave the C_2-symmetric spiro-titanate complex Ti(mbmp)$_2$. The crystalline labile solvent adducts of the dichloro complex Ti(mbmp)Cl_2 with THF and DME were isolated and characterized. A single-crystal X-ray structural analysis revealed the THF adduct to be a mono(THF) adduct with a trigonal-bipyramidal configuration, the bidentate mbmp ligand spanning an apical and equatorial site and the THF ligand occupying the remaining apical position.

Mononuclear titanium complexes Ti(OR)$_2$X$_2$ [(OR)$_2$ = 2,2′-methylenebis(6-*tert*-butyl-4-methylphenoxy) (mbmp); 2,2′-thiobis(6-*tert*-butyl-4-methylphenoxy) (tbmp); X = Cl, O*i*Pr] containing bidentate phenoxy ligands derived from the sterically demanding bis(phenols) mbmpH_2 and tbmpH_2 have been reported to polymerize 1-alkenes, styrene, and 1,3-dienes when activated with methylaluminoxane ("MAO")[1,2]. These soluble titanium phenoxy complexes constitute a new class of homogeneous polymerization catalysts distinct from the well-known *ansa*-metallocene systems that contain two cyclopentadienyl ligands linked by a covalent bridge (Brintzinger-type ligands). In order to rationally control activity, stereoselectivity, and copolymerization behavior of catalysts based on such bidentate phenoxy ligands, detailed information about the coordination sphere around the titanium center is required. To date, however, only a limited number of transition metal complexes containing the mbmp ligand have been documented[3,4]. Mononuclear titanium complexes of the formula Ti(mbmp)X_2 with X = Cl, Me, η^3-BH_4, and X_2 = (η^5-C_5H_5)Cl were reported to display a C_s-symmetric structure in the solid state with a strongly puckered eight-membered chelate ring in a boat conformation[3]. The ^{1}H-NMR chemical shifts for the two methylene protons of the bridge was found to vary considerably as a function of the ligand X, although their relationship with the various conformations of the eight-membered metallacycle remained undefined[5]. In order to obtain more detailed information about the ligand environment of the Ti(mbmp) fragment, we attempted to augment the number of complexes in this series by preparing mbmp complexes previously not described. We report here that the mbmp ligand forms besides mono(ligand) titanium complexes of the general formula Ti(mbmp)X_2(L) (X = anionic ligand, L = two-electron ligand) also a mononuclear bis(ligand) complex (mbmp)$_2$Ti with a spiro-titanate structure.

Results and Discussion

When the easily prepared orange-red dichloro complex Ti(mbmp)Cl_2[3] is treated with halotrimethylsilane Me_3SiX (X = Br, I) in hexane for 3 d, the corresponding red-brown dibromo and dark red diiodo derivatives Ti(mbmp)X_2 (X = Br, I) are cleanly formed. The somewhat moisture-sensitive compounds are isolated in good yields and are characterized by analytical, mass spectral, and NMR-spectroscopic data. Alternatively, the diisopropoxy complex Ti(mbmp)(O*i*Pr)$_2$ (vide infra) can be employed in the reactions with Me_3SiX to give the dihalo complexes in similarly good yields, but at much faster rates.

The dimethyl complex Ti(mbmp)Me_2[3a] was found to be synthesized best by the reaction of Ti(mbmp)Cl_2 with Grignard reagents such as MeMgBr in ether rather than with LiMe. The yellow, highly air- and moisture-sensitive crystals are also temperature- and light-sensitive and cannot be stored for prolonged periods. In the ^{1}H-NMR spectrum ($CDCl_3$, 25°C), the signals for the two inequivalent methyl groups bound to the titanium center appear as two singlets at δ = 1.18 and 1.29 and as quartets at δ = 57.16 and 60.13 in the ^{13}C-NMR spectrum. A NOESY spectrum at 25°C established the complete assignment of the signals in the ^{1}H-NMR spectrum, as summarized in Figure 1. Thus, the TiMe resonance at higher field shows a NOE to the two *tert*-butyl groups of the mbmp ligand as well as to the second methyl group at lower field and can be assigned to the equatorial methyl group. The methyl group resonance at lower field is at close proximity to one of the methylene

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protons of the bridge and therefore must be the one associated with the axial methyl group. Both protons of the bridge, observed as two AB doublets at δ = 3.14 and 3.52, could also be identified. The resonance at higher field is due to the axial hydrogen directed to the titanium center, whereas the signal at lower field is due to the equatorial hydrogen. The latter shows NOEs to the aromatic protons in the 3-position. It can be concluded that the dimethyl complex preferably adopts the boat conformation with the puckered ring in solution at ambient temperature. The barrier to boat-chair interconversion as well as ring inversion is obviously high. For the related dimethyl silicon compound Si(mbbp)Me$_2$ [mbbp = 2,2′-methylenebis(4,6-di-*tert*-butylphenoxy] an activation barrier for the inversion of ΔG^{+} (6°C) = 13.9 kcal mol^{-1} was determined from the coalescence of the two SiMe resonances[5a].

Scheme 1

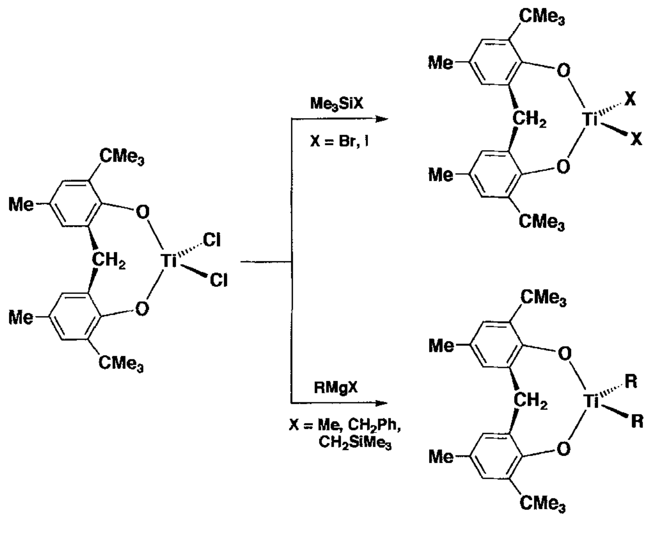
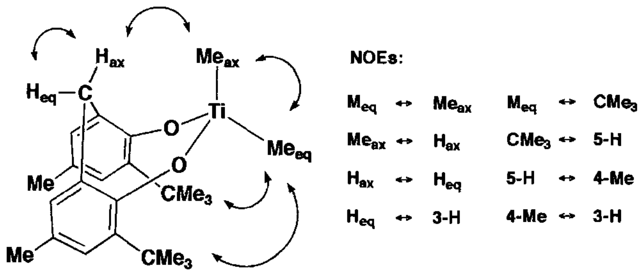


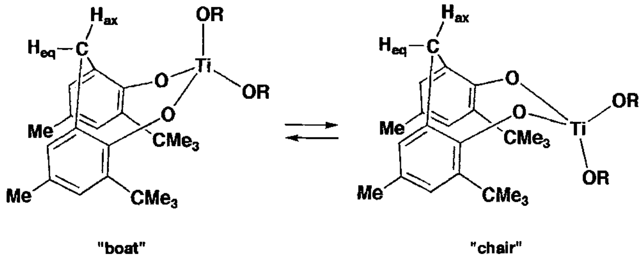
Figure 1. NOESY results for Ti(mbmp)Me$_2$ at 25°C, t_{mix} = 2.0 s



Attempts at fully characterizing the dibenzyl and bis[(trimethylsilyl)methyl] complexes Ti(mbmp)R$_2$ (R = CH$_2$Ph, CH$_2$SiMe$_3$) were hampered so far by the high thermal and light sensitivity of the complexes. However, ^{1}H- and ^{13}C-NMR spectroscopic data indicated formation of the crude products, after reaction between the dichloro complex and the corresponding Grignard reagents. The apparent instability of these higher dialkyl complexes was unexpected[6] and may be related to the steric congestion at the titanium center, rendering the titanium-carbon bonds in these dialkyl derivatives weaker.

The dimethoxy complex Ti(mbmp)(OMe)$_2$ can be prepared by stirring polymeric titanium tetramethoxide with mbmpH$_2$ in hexane and is isolated as orange-red crystals in good yield. A mononuclear structure, analogous to all other complexes of the type Ti(mbmp)X$_2$, is assumed for Ti(mbmp)(OMe)$_2$, based on ^{1}H- and ^{13}C-NMR spectroscopic as well as mass spectral data. While the two methoxy groups give rise to a broad resonance at δ = 4.18 in the ^{1}H-NMR spectrum, two distinct signals at δ = 63.00 and 65.60 are detected in the ^{13}C-NMR spectrum. ^{1}H-NOE measurements reveal that both the methoxy groups are at close proximity to the *tert*-butyl groups, indicating the presence of chair conformers. In contrast to the rigid dimethyl compound Ti(mbmp)Me$_2$, the dimethoxy complex Ti(mbmp)(OMe)$_2$ undergoes a conformational exchange according to Scheme 2.

Scheme 2

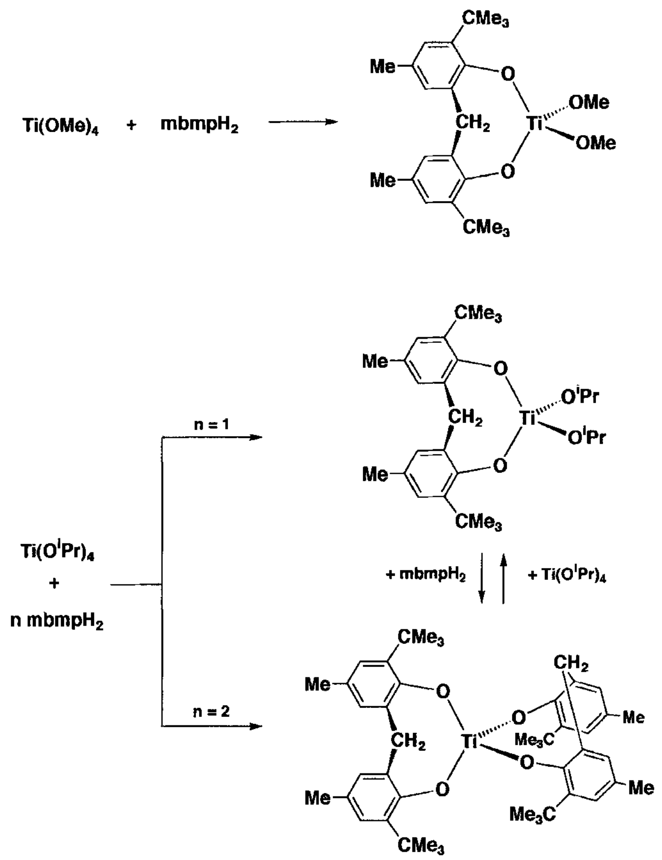


When freshly distilled titanium tetraisopropoxide in ether is treated with precisely one equivalent of mbmpH$_2$ in ether, orange moisture-sensitive crystals of the diisopropoxy complex can be isolated in good yields. As in the case of the Ti(mbmp)(OMe)$_2$ a mononuclear structure is postulated for Ti(mbmp)(O*i*Pr)$_2$, based on ^{1}H- and ^{13}C-NMR spectroscopic as well as mass spectral data. Ti(mbmp)(O*i*Pr)$_2$ is also formed by carefully treating the dimethyl complex Ti(mbmp)Me$_2$ with two equivalents of dry 2-propanol. Analogously, the di-*tert*-butoxy complex Ti(mbmp)(O*t*Bu)$_2$ is isolated as yellow crystals from the reaction of Ti(mbmp)Me$_2$ with a stoichiometric amount of *tert*-butyl alcohol.

During the preparations of the diisopropoxy complex, in particular in the presence of adventitious moisture or upon deliberate hydrolysis of Ti(mbmp)(O*i*Pr)$_2$ with one equivalent of water, we observed the presence of another complex in the reaction mixture. This fairly air- and moisture-stable, pale yellow compound analyzes as Ti(mbmp)$_2$ and can be prepared quantitatively when a solution of titanium tetraisopropoxide is added slowly to two equivalents of mbmpH$_2$ in ether. While mass spectral data establish it to be mononuclear, the appearance of only one set of signals for the mbmp ligand in the ^{1}H- and ^{13}C-NMR spectra reveal that the two mbmp ligands in the molecule are equivalent, but that the molecule does not possess any mirror plane, rendering the two halves of each of the two mbmp ligands inequivalent. Thus, in the ^{1}H-NMR spectrum of Ti(mbmp)$_2$, two signals for 6-CMe$_3$, 4-Me, and four signals for the ring protons are recorded. The methylene bridge give rise to two doublets at δ = 3.78 and 4.54 with $^2J_{\text{HH}}$ =

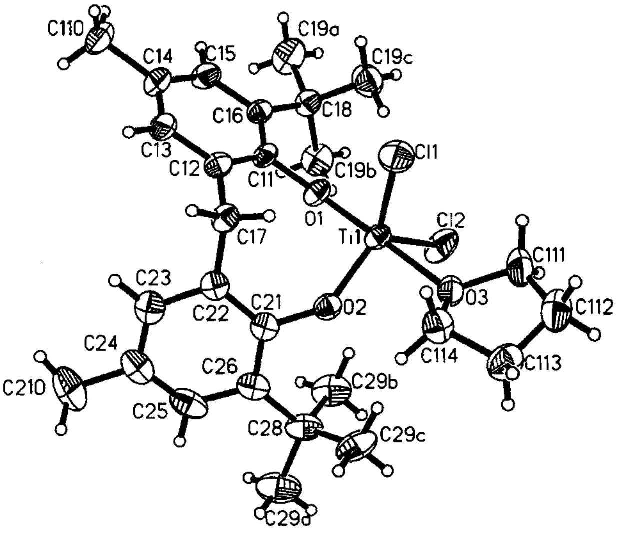
14.8 Hz. Likewise, in the ^{13}C-NMR spectrum all signals of the mbmp ligand except the one due to the methylene bridge (δ = 35.61) are no longer enantiotopic. This somewhat unusual symmetry is in agreement with a C_2 point group for the molecule. The proposed structure was confirmed for the ether solvate of $Ti(mbmp)_2$ by a single-crystal X-ray structural analysis, although the structure could not be refined satisfactorily due to severe disorder problems of the lattice solvent[7]. Nonetheless, the chiral molecule was shown to clearly contain a C_2-symmetry axis relating the two enantiotopic moieties of each of the mbmp ligand. The titanium center is in a regular tetrahedral environment, and a boat conformation is adopted by both rings. Few mononuclear bis(diolato) titanium complexes with spirocyclic structure have been structurally characterized[8].

Scheme 3



In order to probe more precisely the Lewis acidity of the titanium center coordinated to the mbmp ligand, the adduct formation of the dichloro complex $Ti(mbmp)Cl_2$[3a] was reinvestigated. $Ti(mbmp)Cl_2$ dissolves in ether with concomitant color change from orange to red, but no adduct could be isolated. On the other hand, a THF adduct was easily obtained as dark red crystals by treating an ethereal solution of $Ti(mbmp)Cl_2$ with excess THF or simply by concentrating a THF solution of $Ti(mbmp)Cl_2$. From analytical, mass spectral, and NMR-spectroscopic data the number of the coordinated molecules could not be determined unambiguously. Whereas well-shaped crystals clearly contained more than one molecule of THF, vacuum-dried samples indicated the presence of exactly one THF per titanium. Upon heating in vacuo all THF is lost, and the parent dichloro complex $Ti(mbmp)Cl_2$ is recovered. The results of an X-ray structural analysis of a single crystal revealed the presence of a mono(THF) adduct with a pentacoordinated titanium center (Figure 2). In addition, the lattice contains one disordered ether molecule per 4 molecules of the adduct. The titanium atom adopts a regular trigonal-bipyramidal geometry. Whereas the two chloro ligands and one oxygen atom of the bidentate ligand occupy the equatorial positions, the apical sites are taken by the oxygen atoms of the THF and the second oxygen atom of the mbmp ligand. The lengths of the apical and equatorial titanium-oxygen bonds of the mbmp ligand are 1.774(2) and 1.808(2) Å, respectively. They are in the expected range for titanium(IV) alkoxy complexes where phenoxy ligands are not bridging[3,9–13], but clearly distinct from each other. The shorter bond between titanium and the apical oxygen is coupled with the wider bond angle at the oxygen atom of 152.0(2)°, indicative of a more pronounced double bond character as compared to the equatorial oxygen atom with an angle of 139.3(2)°. The bite angle of the mbmp ligand at the titanium is 96.2(1)° and significantly smaller than that in the parent dichloro complex of 106.5(2)°. It is quite obvious that the chelating mbmp ligand has to undergo significant distortion in order to accommodate a fifth ligand at the titanium center. The equatorial oxygen of the ligand therefore is hindered from being as strongly π-donating as the apical oxygen[9]. The two titanium-chlorine bond lengths of 2.258(1) and 2.275(1) Å are longer by ca. 0.05 Å than those found in $Ti(mbmp)Cl_2$ [2.215(2), 2.206(2) Å].

Figure 2. ORTEP diagram for one of the two independent molecules of $Ti(mbmp)Cl_2(THF)$



Solutions of $Ti(mbmp)Cl_2(THF)$ in the presence of excess THF show only one set of resonances for the THF protons even at temperatures as low as −80°C, indicating a rapid exchange between free THF and THF coordinated to the titanium center in $Ti(mbmp)Cl_2$. On the NMR time scale, therefore, the molecule retains a mirror plane, and the two moieties of the mbmp ligand appear equivalent. For the exchange process, both a dissociative and an associative mechanism is conceivable. As depicted in Scheme 4, the coordination of the THF from each of the enantiotopic sides of the C_s-symmetric dichloro complex results in the formation of enantiomeric isomers with the THF molecule occupying the axial site. The formation of enantiomeric pairs of diastereomers formally resulting from the attack of the THF either from the "top" or "bottom" is not preferred due to steric hindrance by the methylene bridge and the two *tert*-butyl groups, respectively. Moreover, these sterically hindered isomers may convert into the above isomers by a facile "turnstile" rearrangement of the three monodentate ligands.

Table 1. Selected bond lengths [Å] and angles [°] of Ti(mbmp)Cl_2(THF)

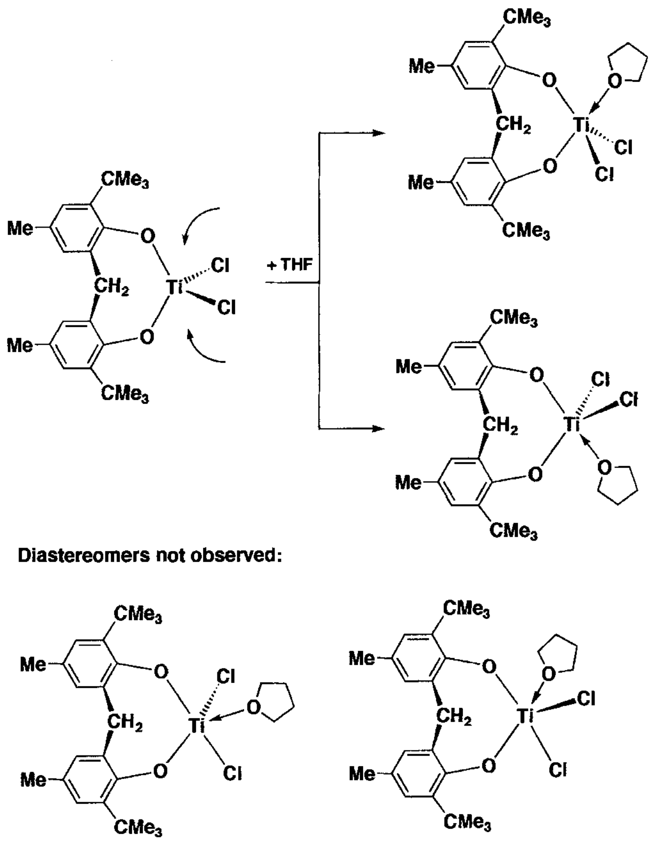
Ti1-O1	1.774(2)	Ti1-O2	1.808(3)
Ti1-O3	2.163(3)	Ti1-Cl1	2.275(1)
Ti1-Cl2	2.258(1)	C11-O1	1.365(4)
C12-O2	1.379(4)	C11-C12	1.394(5)
C12-C17	1.513(5)	C12-C13	1.388(5)
C13-C14	1.372(5)	C14-C15	1.387(6)
C15-C16	1.392(5)	C11-C16	1.409(5)
C17-C22	1.516(5)	C22-C23	1.400(5)
C23-C24	1.379(6)	C24-C25	1.376(6)
C25-C26	1.405(6)	C21-C26	1.414(5)
O1-Ti1-O2	96.2(1)	O1-Ti1-Cl1	92.2(1)
O1-Ti1-Cl2	98.8(1)	O2-Ti1-Cl1	121.2(1)
O2-Ti1-Cl2	116.6(1)	Cl1-Ti1-Cl2	119.3(1)
O2-Ti1-O3	83.5(1)	O3-Ti1-Cl1	83.1(1)
O3-Ti1-Cl2	86.5(1)	Ti1-O1-C11	152.0(2)
Ti1-O2-C21	139.3(2)	O1-C11-Cl2	117.2(3)
C11-C12-C17	121.3(3)	C12-C17-C22	113.4(3)
C17-C22-C21	123.5(3)	O2-C21-C22	119.0(3)

Bidentate DME forms also an adduct Ti(mbmp)Cl_2-(DME) according to elemental analysis and NMR-spectroscopic data. A six-coordinate titanium center is assumed for this complex. However, due to the rapid exchange process of the DME ligand in solution the exact coordination sphere remains uncertain. We do not exclude that in analogy to the THF adduct the DME is bound only by one oxygen.

The sterically congested environment of the mbmp ligand around the titanium is quite unusual in that the Lewis acidity of the formally eight-electron metal center is suppressed. Similar complexes of the formula "Ti$(OR)_2Cl_2$" are dinuclear with μ-OR bridges (R = Ph[10a], Et[10b]; $(OR)_2$ = 2-methyl-2,4-pentanediolato[11]; $(OR)_2$ = 3,3'-dimethyl-1,1'-bi-2-naphtholato[12a]) or form an octahedral bis(THF) adduct (R = 2,6-$Me_2C_6H_3$[13a]). In contrast to the dichloro complex Ti(mbmp)Cl_2, the dibromo and diiodo complexes do not form isolable Lewis adducts with THF. Likewise the dialkyl and dialkoxy complexes do not interact with THF as judged by ^{1}H-NMR spectroscopy.

The ^{1}H-chemical shift difference $\Delta\delta = \delta(H_{ax}) - \delta(H_{eq})$ for the two methylene protons of the bridge in the mbmp titanium complexes was earlier suggested to be a probe for the coordination sphere within a mbmp complex[3a]. The ^{1}H-NMR spectroscopic data for the methylene hydrogen atoms are compiled in Table 2. For the complexes with X = Cl, Me, OMe, O*i*Pr the assignment is based on NOESY spectra and can be considered to be unambiguous. It is evident that the resonance for the pseudo-axial proton H_{ax} close to the metal fragment is subject to a broader variation. This can result even in an "inversion" of the order for $\delta(H_{ax})$ and $\delta(H_{eq})$ as in the case of Ti(mbmp)Me_2. The pseudo-equatorial proton H_{eq}, turned away from the metal center, resonate in a narrower range. Qualitatively, the variation of Δδ appears to be a function of the electronegativity. The geminal coupling constants have values in the range of 13.6–14.8 Hz and the values for $^1J_{CH}$ is in the range of 120 Hz, suggesting that the rigid mbmp ligand framework is not very sensitive to the change of the metal fragment. Moreover, NMR-spectroscopic data of the conformationally more flexible ali- and heterocyclic compounds show that the data for the Ti(mbmp) complexes are not exceptional[14]. The fact that Ti(mbmp) complexes prefer the boat conformation over the boat-chair conformation usually encountered in eight-membered ring systems[5,14,15] has to be a consequence of the repulsive 6-*tert*-butyl groups of the mbmp ligand.

Scheme 4



In conclusion, it has become apparent that the steric constraint the mbmp ligand exerts on the titanium center is due to the methylene bridge as well as the two *tert*-butyl groups resulting in a preference for the rigid boat conformation in the solid state. The ^{1}H-chemical shifts of the methylene protons are influenced by the ligands coordinated at the titanium, but not so much by the conformation. We are presently involved in studies aimed at elucidating the effect of

Table 2. ^{1}H-NMR spectroscopic data ($CDCl_3$, 25°C) for the methylene bridge in transition metal mbmp complexes

Compound	$\delta(H_{ax})$	$\delta(H_{eq})$	$\Delta\delta = \delta(H_{ax}) - \delta(H_{eq})$	$\lvert ^2J_{HH} \rvert$
$Ti(mbmp)Cl_2$	4.11	3.73	1.04	14.4
$Ti(mbmp)Br_2$	4.34	3.58	0.76	14.2
$Ti(mbmp)I_2$	3.86	3.59	0.27	14.4
$Ti(mbmp)Me_2$	3.14	3.52	-0.38	14.3
$Ti(mbmp)Ph_2$	3.56	3.72	-0.16	14.5
$Ti(mbmp)(CH_2Ph)_2$	2.94	3.06	-0.12	14.4
$Ti(mbmp)(CH_2SiMe_3)_2$	3.15	3.47	-0.32	14.2
$Ti(mbmp)CpCl$[a)]	4.16	3.44	0.72	13.6
$Ti(mbmp)(BH_4)_2$[b)]	4.66	3.22	1.44	13.9
$Ti(mbmp)(OMe)_2$	4.16	3.35	0.81	13.9
$Ti(mbmp)(O^iPr)_2$	4.29	3.47	0.82	14.0
$Ti(mbmp)(O^tBu)_2$	4.32	3.42	0.90	14.0
$Ti(mbmp)_2$	4.54	3.78	0.76	14.8
$Ti(mbmp)Cl_2(THF)$	4.65	3.40	1.25	13.6
$Ti(mbmp)Cl_2(DME)$	4.57	3.45	1.12	13.6
$Ti(mbmp)Cl_2(^tBuNC)$[a)]	4.52	3.49	1.03	13.9
$Zr(mbmp)(BH_4)_2(THF)$[b)]	4.81	3.59	1.59	13.7
$V(mbmp)(=O)Cl$[c)]	4.78	3.22	1.56	14.5
$V(mbmp)(=O)(CH_2SiMe_3)$[c)]	4.71	3.63	1.08	14.1

[a)] In CD_2Cl_2; ref.[3a]. – [b)] In C_6D_6; ref.[3b]. – [c)] In C_6D_6; ref.[4].

the bridge on the metal-centered reactivity of chelate complexes of similar types. To this end, we have already prepared a series of bis(phenols) of the general type 2,2′-Z(6-*t*Bu-4-$MeC_6H_2OH)_2$ containing various bridges Z other than the methylene group[7].

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Experimental

All experiments were carried out under dry argon by using standard Schlenk technique. Solvents were purified, dried, and distilled under argon. – ^{1}H and ^{13}C NMR: Bruker ARX 200, AC 300 or AMX 500. – IR: Nicolet FT-5-DX. – MS: Varian CH 7. – Elemental analyses: Microanalytical laboratory of this department.

Dichloro[2,2′-methylenebis(6-tert-butyl-4-methylphenoxy)]-titanium: To a solution of 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) (18.0 g, 53.0 mmol) in 250 ml of hexane was added titanium tetrachloride (5.8 ml, 53.0 mmol) and the orange mixture stirred at room temp. for 24 h. Cooling to −20°C for 18 h and filtration through a glass frit afforded orange-red microcrystals after drying in vacuo; yield 22.1 g (91%). – ^{1}H NMR ($CDCl_3$, 25°C): δ = 1.48 [s, 18H, $C(CH_3)_3$], 2.36 (s, 6H, 4-CH_3), 3.73 [d, $^2J_{HH}$ = 14.4 Hz, 1H, CH_2(eq)], 4.11 [d, $^2J_{HH}$ = 14.4 Hz, 1H, CH_2(ax)], 7.01 (d, $^4J_{HH}$ = 1.8 Hz, 2H, 5-H), 7.20 (d, $^4J_{HH}$ = 1.8 Hz, 2H, 3-H). – ^{13}C NMR ($CDCl_3$, 25°C): δ = 21.57 (q, $^1J_{CH}$ = 127 Hz, 4-CH_3), 30.70 [q, $^1J_{CH}$ = 126 Hz, $C(\mathit{C}H_3)_3$], 35.69 [s, $\mathit{C}(CH_3)_3$], 35.72 (t, $^1J_{CH}$ = 128 Hz, CH_2), 126.62 (d, $^1J_{CH}$ = 156 Hz, C-5), 129.30 (d, $^1J_{CH}$ = 155 Hz, C-3), 135.78 (s, C-4), 136.73 (s, C-6), 138.44 (s, C-2), 165.20 (s, C-1). – IR (Nujol): $\tilde{\nu}$ = 1219 cm^{-1} m, 1204 m, 1109 w, 918 m, 630 w, 470 m, 434 w, 412 m, 363 w. – EI-MS, *m/z* (%): 456 (94) [M^+], 441 (58) [$M^+ - CH_3$], 405 (37) [M^+ – Cl, CH_3], 389 (11) [M^+ – Cl, 2 CH_3], 57 (100) [$C_4H_9^+$]. – $C_{23}H_{30}Cl_2O_2Ti$ (457.3): calcd. C 60.41, H 6.61; found C 60.48, H 6.58.

Dibromo[2,2′-methylenebis(6-tert-butyl-4-methylphenoxy)]-titanium: To a solution of diisopropoxy[2,2′-methylenebis(6-*tert*-butyl-4-methylphenoxy)]titanium (0.99 g, 1.96 mmol) in 10 ml of dichloromethane was slowly added bromotrimethylsilane (0.51 ml, 3.91 mmol) at room temp. After completion of the addition the reaction mixture was stirred for 4 h at room temp. Evaporation of the solvent and washing with hexane afforded brown-red microcrystals; yield 0.71 g (67%). – ^{1}H NMR ($CDCl_3$, 25°C): δ = 1.49 [s, 18H, $C(CH_3)_3$], 2.32 (s, 6H, 4-CH_3), 3.58 [d, $^2J_{HH}$ = 14.2 Hz, 1H, CH_2(eq)], 4.34 [d, $^2J_{HH}$ = 14.2 Hz, 1H, CH_2(ax)], 6.97 (d, $^4J_{HH}$ = 1.8 Hz, 2H, 5-H), 7.13 (d, $^4J_{HH}$ = 1.8 Hz, 2H, 3-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C): δ = 21.21 (4-CH_3), 30.52 [$C(\mathit{C}H_3)_3$], 35.18 [$\mathit{C}(CH_3)_3$], 35.66 (C-7), 125.72 (C-3), 128.83 (C-3), 134.13 (C-4), 136.36 (C-6), 138.73 (C-2), 166.37 (C-1). – EI-MS, *m/z* (%): 544 (19) [M^+], 529 (11) [$M^+ - CH_3$], 449 (13) [M^+ – Br, CH_3], 257 (10), 57 (100) [$C_4H_9^+$]. – $C_{23}H_{30}Br_2O_2Ti$ (547.4): calcd. C 50.58, H 5.54; found C 50.46, H 5.77.

Diiodo[2,2′-methylenebis(6-tert-butyl-4-methylphenoxy)]-titanium was prepared from diisopropoxy[2,2′-methylenebis(6-*tert*-butyl-4-methylphenoxy)]titanium by using Me_3SiI analogously to the dibromo complex and isolated as a dark red powder, yield 75%. – ^{1}H NMR ($CDCl_3$, 25°C): δ = 1.51 [s, 18H, $C(CH_3)_3$], 2.25 (s, 6H, 4-CH_3), 3.59 [d, $^2J_{HH}$ = 14.4 Hz, 1H, CH(eq)], 3.86 [d, $^2J_{HH}$ = 14.4 Hz, 1H, CH_2(ax)], 6.94 (d, $^4J_{HH}$ = 1.8 Hz, 2H, 5-H), 7.11 (d, $^4J_{HH}$ = 1.8 Hz, 2H, 3-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C): δ = 21.25 (4-CH_3), 30.65 [$C(\mathit{C}H_3)_3$], 35.45 [$\mathit{C}(CH_3)_3$], 36.42 (CH_2), 125.91 (C-3), 134.63 (C-3), 135.87 (s, C-4), 136.36 (s, C-6), 138.46 (s, C-2), 165.86 (s, C-1). – EI-MS, *m/z* (%): 640 (62) [M^+], 625 (13) [$M^+ - CH_3$], 513 (9) [M^+ – I], 498 (26) [M^+ – I, CH_3], 481 (7) [M^+ – I, 2 CH_4], 441 (8) [M^+ – I, C_4H_8], 128 (13) [HI^+], 57 (100) [$C_4H_9^+$]. – $C_{23}H_{30}I_2O_2Ti$ (640.2): calcd. C 43.15, H 4.72; found C 43.62, H 4.88.

Dimethyl[2,2′-methylenebis(6-tert-butyl-4-methylphenoxy)]-titanium: To a solution of dichloro[2,2′-methylenebis(6-*tert*-butyl-4-methylphenoxy)]titanium (4.15 g, 9.06 mmol) in 120 ml of ether was slowly added methylmagnesium bromide (6.32 ml of a 2.86 M solution, 18.08 mmol) at −78°C. After completion of the addition the reaction mixture was stirred for 1 h at −78°C and allowed to warm up slowly. After addition of 1.5 ml of dioxane the mixture was filtered and the filter bed thoroughly washed with ether. Evaporation of the solvent and washing with hexane afforded yellow crystals, yield 3.14 g (83%). – ^{1}H NMR ($CDCl_3$, 25°C): δ = 1.18 [s, 3H, $TiCH_3$(eq)], 1.29 [s, 3H, $TiCH_3$(ax)], 1.55 [s, 18H, $C(CH_3)_3$], 2.27 (s, 6H, 4-CH_3), 3.14 [d, $^2J_{HH}$ = 14.3 Hz, 1H, CH_2(ax)], 3.52 [d, $^2J_{HH}$ = 14.3 Hz, 1H, CH_2(eq)], 6.96 (d, $^4J_{HH}$ = 1.8 Hz, 2H, 5-H), 7.10 (d, $^4J_{HH}$ = 1.8 Hz, 2H, 3-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C): δ = 20.96 (4-CH_3), 30.65 [$C(\mathit{C}H_3)_3$], 35.45 (CH_2), 36.42 [$\mathit{C}(CH_3)_3$], 57.16 [$TiCH_3$(ax)], 60.31 [$TiCH_3$(eq)], 125.91 (C-5), 128.91 (C-3), 134.63 (C-4), 135.87 (C-6), 138.46 (C-2), 165.86 (C-1). – EI-MS, *m/z* (%): 416 (19) [M^+], 386 (100) [M^+ – 2 CH_3], 177 (11) [$C_{12}H_{17}O$].

Dimethoxy[2,2′-methylenebis(6-tert-butyl-4-methylphenoxy)]-titanium: A suspension of solid titanium tetramethoxide (0.87 g, 8.05 mmol) and 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) in 15 ml of hexane is stirred for 3 d at room temp. Filtration, washing with hexane, and drying in vacuo gave orange-red microcrystals, yield 3.25 g (97%). – ^{1}H NMR ($CDCl_3$, 25°C): δ = 1.37 [s, 18H, $C(CH_3)_3$], 2.20 (s, 6H, 4-CH_3), 3.35 [d, $^2J_{HH}$ = 13.9 Hz, 1H, CH_2(eq)], 4.16 [d, $^2J_{HH}$ = 13.9 Hz, 1H, CH_2(ax)], 4.18 (s, 6H, OCH_3), 6.82 (d, $^4J_{HH}$ = 1.8 Hz, 2H, 5-H), 6.90 (d, $^4J_{HH}$ = 1.8 Hz, 2H, 3-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C): δ = 20.87 (4-CH_3), 29.88 [$C(\mathit{C}H_3)_3$], 34.72 [$\mathit{C}(CH_3)_3$], 34.82 (CH_2), 63.00, 65.60 (OCH_3), 125.15 (C-5), 128.08 (C-3), 129.61 (C-4), 135.30 (C-6), 139.95 (C-2), 160.31 (C-1). – EI-MS, *m/z* (%): 448 (100) [M^+], 433

(18) $[M^+ - CH_3]$, 416 (12) $[M^+ - CH_3OH]$, 401 (53) $[M^+ - CH_3OH, CH_3]$, 385 (12) $[M^+ - CH_3OH, CH_3O]$, 345 (23) $[M^+ - CH_3OH, C_4H_8, CH_3]$, 209 (20) $[C_{15}H_{13}O^+]$, 193 (18) $[C_{15}H_{13}^+]$, 57 (38) $[C_4H_9^+]$. – FD-MS, *m/z* (%): 448 $[M^+]$. – $C_{23}H_{36}O_4Ti$ (448.5): calcd. C 66.96, H 8.09; found C 67.05, H 8.30.

Diisopropoxy[2,2'-methylenebis(6-tert-butyl-4-methylphenoxy)]-titanium: To freshly distilled titanium tetraisopropoxide (1.5 ml, 1.46 g, 5.12 mmol) in 20 ml of ether was added dropwise 2,2'-methylenebis(6-*tert*-butyl-4-methylphenol) in 20 ml of ether at 0°C. After concentrating the mixture to 5 ml, followed by cooling to −20°C, orange crystals were filtered off, yield 2.25 g (92%). – ^1H NMR ($CDCl_3$, 25°C): δ = 1.33 [d, $^3J_{HH}$ = 6.1 Hz, 12H, $CH(CH_3)_2$] 1.39 [s, 18H, $C(CH_3)_3$], 2.26 (s, 6H, 4-CH_3), 3.47 [d, $^2J_{HH}$ = 14.0 Hz, 1H, CH_2(eq)], 4.29 [d, $^2J_{HH}$ = 14.0 Hz, 1H, CH_2(ax)], 4.63 [br. sep, 1H, $CH(CH_3)_2$], 4.74 [sep, $^3J_{HH}$ = 6.1 Hz, 1H, $CH(CH_3)_2$], 6.89 (d, $^4J_{HH}$ = 2.1 Hz, 2H, 5-H), 7.06 (d, $^4J_{HH}$ = 2.1 Hz, 2H, 3-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C): δ = 21.10 (4-CH_3), 26.58 [$CH(CH_3)_2$], 30.13 [$C(CH_3)_3$], 34.02 (CH_2), 35.00 [$C(CH_3)_3$], 79.33 [$CH(CH_3)_2$], 125.56 (C-5), 128.60 (C-3), 129.92 (C-4), 133.47 (C-6), 136.48 (C-2), 159.69 (C-1). – EI-MS, *m/z* (%): 504 (100) $[M^+]$, 489 (4) $[M^+ - CH_3]$, 444 (5) $[M^+ - C_3H_7OH]$, 429 (12) $[M^+ - C_3H_7OH, CH_3]$, 57 (12) $[C_4H_9^+]$. – FD-MS, *m/z* (%): 504 $[M^+]$. – $C_{29}H_{44}O_4Ti$ (504.6): calcd. C 69.03, H 8.79; found C 68.42, H 8.72.

Di-tert-butoxy[2,2'-methylenebis(6-tert-butyl-4-methylphenoxy)]titanium: A solution of the dimethyl complex (0.44 g, 1.06 mmol) in 15 ml of ether was treated dropwise with *tert*-butyl alcohol (0.125 ml, 2.13 mmol) and stirred for 4 h at room temp. Removal of all volatile compounds in vacuo, washing with hexane, and drying in vacuo gave yellow microcrystals, yield 0.35 g (62%). – ^1H NMR ($CDCl_3$, 25°C): δ = 1.36 [s, 18H, 6-$C(CH_3)_3$], 1.48 [s, 18H, $OC(CH_3)_3$], 2.21 (s, 6H, 4-CH_3), 3.42 [d, $^2J_{HH}$ = 14.0 Hz, 1H, CH_2(eq)], 4.32 [d, $^2J_{HH}$ = 14.0 Hz, 1H, CH_2(ax)], 6.84 (d, $^4J_{HH}$ = 1.8 Hz, 2H, 5-H), 7.02 (d, $^4J_{HH}$ = 1.8 Hz, 2H, 3-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C): δ = 21.08 (4-CH_3), 30.12 [$C(CH_3)_3$], 31.25 [$C(CH_3)_3$], 32.16, 32.41 [$OC(CH_3)_3$], 35.05 (CH_2), 66.09, 68.21 [$OC(CH_3)_3$], 125.52 (C-5), 128.57 (C-3), 129.65 (C-4), 133.85 (C-6), 136.44 (C-2), 160.47 (C-1). – EI-MS, *m/z* (%) = 532 (5) $[M^+]$, 379 (23) $[M^+ - CH_3]$, 59 (90) $[C_3H_7O^+]$, 57 (100) $[C_4H_9^+]$. – $C_{25}H_{40}O_4Ti$ (532.5): calcd. C 69.91, H 9.08; found C 68.22, H 8.09.

Bis[2,2'-methylenebis(6-tert-butyl-4-methylphenoxy)]titanium: To a solution of 2,2'-methylenebis(6-*tert*-butyl-4-methylphenol) (2.33 g, 6.84 mmol) in 20 ml of ether was added freshly distilled titanium tetraisopropoxide (1.0 ml, 3.41 mmol) at room temp. The reaction mixture was stirred 2 h at room temp. After removing all volatile compounds the crude product was dried at 120°C to give yellow microcrystals, yield 2.45 g (99%). – ^1H NMR ($CDCl_3$, 25°C): δ = 1.30, 1.37 [s, 18H, $C(CH_3)_3$], 2.27, 2.33 (s, 6H, 4-CH_3), 3.78 [d, $^2J_{HH}$ = 14.8 Hz, 1H, CH_2(eq)], 4.54 [d, $^2J_{HH}$ = 14.8 Hz, 1H, CH_2(ax)], 6.91, 6.95 (d, $^4J_{HH}$ = 1.9 Hz, 2H, 5-H), 7.10, 7.15 (d, $^4J_{HH}$ = 1.9 Hz, 2H, 3-H). – ^{13}C NMR ($CDCl_3$, 25°C): δ = 0.98 (q, $^1J_{CH}$ = 126 Hz, 4-CH_3), 29.99, 30.20 [q, $^1J_{CH}$ = 126 Hz, $C(CH_3)_3$], 34.64, 35.04 [s, $C(CH_3)_3$], 35.61 (t, $^1J_{CH}$ = 125 Hz, CH_2), 125.61, 125.83 (d, $^1J_{CH}$ = 155 Hz, C-5), 128.12, 128.73 (d, $^1J_{CH}$ = 153 Hz, C-3), 131.21, 131.37 (s, C-4), 133.82, 134.88 (s, C-6), 136.25 (s, C-2), 160.18, 160.69 (s, C-1). – IR (Nujol): $\tilde{\nu}$ = 1432 cm^{-1} m, 1224 s, 1137 m, 905 w, 864 s, 625 m, 439 w, 401 w, 315 w. – EI-MS, *m/z* (%): 724 (100) $[M^+]$, 57 (31) $[C_4H_9^+]$. – $C_{46}H_{60}O_4Ti$ (724.9): calcd. C 76.22, H 8.34; found C 75.96, H 8.42.

Dichloro(1,2-dimethoxyethane)[2,2'-methylenebis(6-tert-butyl-4-methylphenoxy)]titanium: A solution of dichloro[2,2'-methylenebis(6-*tert*-butyl-4-methylphenoxy)]titanium (0.45 g, 0.98 mmol) in 15 ml of 1,2-dimethoxyethane was concentrated to ca. 1 ml. The dark red crystals were filtered, washed with hexane, and dried in vacuo; yield 0.52 g (97%). – ^1H NMR ($CDCl_3$, 25°C): δ = 1.48 [s, 18H, $C(CH_3)_3$], 2.30 (s, 6H, 4-CH_3), 3.45 [d, $^2J_{HH}$ = 13.6 Hz, 1H, CH_2(eq)], 3.73 (s, 6H, OCH_3), 3.85 (m, 4H, CH_2O), 4.57 [d, $^2J_{HH}$ = 13.6 Hz, 1H, CH_2(ax)], 6.95 (d, $^4J_{HH}$ = 1.8 Hz, 2H, 5-H), 7.13 (d, $^4J_{HH}$ = 1.8 Hz, 2H, 3-H). – ^{13}C NMR ($CDCl_3$, 25°C): δ = 21.39 (q, $^1J_{CH}$ = 126 Hz, 4-CH_3), 31.07 [q, $^1J_{CH}$ = 126 Hz, $C(CH_3)_3$], 35.31 [s, $C(CH_3)_3$], 35.43 (t, $^1J_{CH}$ = 126 Hz, CH_2), 62.37 (q, $^1J_{CH}$ = 126 Hz, OCH_3), 72.30 (t, $^1J_{CH}$ = 126 Hz, OCH_2), 126.08 (d, $^1J_{CH}$ = 156 Hz, C-5), 128.98 (d, $^1J_{CH}$ = 155 Hz, C-3), 133.77 (s, C-4), 137.59 (s, C-6), 139.74 (s, C-2), 165.00 (s, C-1). – $C_{27}H_{40}Cl_2O_4Ti$ (547.4): calcd. C 59.24, H 7.37; found C 58.70, H 7.06.

Dichloro[2,2'-methylenebis(6-tert-butyl-4-methylphenoxy)]-(tetrahydrofuran)titanium: A solution of dichloro[2,2'-methylenebis(6-*tert*-butyl-4-methylphenoxy)]titanium (0.45 g, 0.98 mmol) in 15 ml of THF was concentrated to ca. 1 ml. The dark red crystals were filtered, washed with hexane, and dried in vacuo; yield 0.52 g (97%). – ^1H NMR ($CDCl_3$, 25°C): δ = 1.41 [s, 18H, $C(CH_3)_3$], 1.98 (m, 4H, β-CH_2), 2.25 (s, 6H, 4-CH_3), 3.40 [d, $^2J_{HH}$ = 14.0 Hz, 1H, CH_2(eq)], 4.14 (m, 4H, α-CH_2), 4.65 [d, $^2J_{HH}$ = 14.0 Hz, 1H, CH_2(ax)], 6.91 (d, $^4J_{HH}$ = 1.8 Hz, 2H, 5-H), 7.03 (d, $^4J_{HH}$ = 1.8 Hz, 2H, 3-H). – ^{13}C NMR ($CDCl_3$, 25°C): δ = 21.41 (q, $^1J_{CH}$ = 126 Hz, 4-CH_3), 25.82 (t, $^1J_{CH}$ = 136 Hz, OCH_2CH_2), 30.57 [q, $^1J_{CH}$ = 126 Hz, $C(CH_3)_3$], 35.20 [s, $C(CH_3)_3$], 35.48 (t, $^1J_{CH}$ = 125 Hz, CH_2), 71.03 (t, $^1J_{CH}$ = 149 Hz, OCH_2), 125.62 (d, $^1J_{CH}$ = 150 Hz, C-5), 128.94 (d, $^1J_{CH}$ = 154 Hz, C-3), 133.28 (s, C-4), 137.00 (s, C-6), 139.20 (s, C-2), 165.20 (s, C-1). – $C_{27}H_{38}Cl_2O_3Ti$ (529.4): calcd. C 61.26, H 7.24; found C 61.00, H 7.00.

X-Ray Crystal Structure Analysis of Ti(mbmp)Cl₂(THF) · 1/4 Et₂O: Red-brown platelets were obtained by slow cooling a solution of $Ti(mbmp)Cl_2$ in Et_2O/THF. Cell dimensions and intensity data were obtained with an Enraf-Nonius CAD-4 diffractometer: $C_{28}H_{40.25}Cl_2O_{3.25}Ti$, M = 547.7, a = 943.1(2), b = 1835.6(4), c = 1899.2(4) pm, α = 66.58(3), β = 87.61(3), γ = 75.28(3)°, Z = 4, $d_{calc.}$ = 1.250 Mgm^{-3}, triclinic, $P\bar{1}$, Cu-K_α (λ = 154.178 pm), graphite monochromator, 0.48 × 0.24 × 0.10 mm, T = 193 K, 2.54° < Θ < 54.96°, $F(000)$ = 1162. Number of reflections measured 7731, 7196 independent reflections [R(int) = 0.0526] of which 6282 were assigned observed [$I > 2\sigma(I)$], absorption coefficient 4.384 mm^{-1}. The structure was solved by direct methods and difference Fourier synthesis and refined against all F^2 data (SHELX-86[16a], SHELXL-93[16b]). The structure contains two independent molecules, one of which showing orientational disorder of the THF carbon atoms. In addition, a disordered ether molecule is positioned at the inversion center (0.5, 0, 0). All nonhydrogen atoms except two carbon atoms of the disordered ether molecule were refined with anisotropic temperature factors. Hydrogen atoms were calculated at their idealized positions except those of disordered groups. The refinement converged at residuals $wR2$ = 0.1464 for all reflections, corresponding to a conventional R = 0.050 for the observed F_o data. The residual electron density was 0.56 $e\AA^{-3}$.

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[1] M. Kakugo, T. Miyatake, K. Mizunuma, *Chem. Express* **1987**, *2*, 445; T. Miyatake, K. Mizunuma, Y. Seki, M. Kakugo, *Makromol. Chem., Rapid Commun.* **1989**, *10*, 349; T. Miyatake, K. Mizunuma, M. Kakugo, *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 203.

[2] C. J. Schaverien, A. J. van der Linden, A. G. Orpen, *Am. Chem. Soc., Polym. Div., Polymer Prepr.* **1994**, *35*, 672.

[3] [3a] C. Floriani, F. Corazza, W. Lesueur, A. Chiesi-Villa, C. Gua-

stini, *Angew. Chem.* **1989**, *101*, 93; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 66. – [3b] F. Corazza, C. Floriani, A. Chiesi-Villa, C. Guastini, *Inorg. Chem.* **1991**, *30*, 146. – [3c] E. Barren, P. J. Toscano, S. Liu, J. Zubieta, unpublished results.

[4] [4a] M. Mazzanti, C. Floriani, A. Chiesi-Villa, C. Guastini, *J. Chem. Soc., Dalton Trans.* **1989**, 1793. – [4b] P. J. Toscano, E. J. Schermerhorn, C. Dettelbacher, D. Macherone, J. Zubieta, *J. Chem. Soc., Chem. Commun.* **1991**, *933*. – [4c] E. J. Schermerhorn, Master's Thesis, State University of New York at Albany, **1993**. For a dinuclear molybdenum and tungsten complex, see: M. H. Chisholm, I. P. Parkin, K. Folting, E. B. Lubkovsky, W. E. Streib, *J. Chem. Soc., Chem. Commun.* **1991**, 1673.

[5] [5a] S. D. Pastor, J. D. Spivack, *J. Org. Chem.* **1984**, *49*, 1297. – [5b] R. O. Day, T. K. Prakasha, R. R. Holmes, H. Eckert, *Organometallics* **1994**, *13*, 1285.

[6] R. W. Chestnut, L. D. Durfee, P. E. Fanwick, I. P. Rothwell, K. Folting, J. C. Huffman, *Polyhedron* **1987**, 2019.

[7] [7a] S. Fokken, W. Massa, J. Okuda, unpublished results. – [7b] S. Fokken, Diplomarbeit, Universität Marburg, **1994**.

[8] D. Seebach, D. A. Plattner, A. K. Beck, Y. M. Wang, D. Hunziker, W. Petter, *Helv. Chim. Acta* **1992**, *75*, 2171; M. B. Hursthouse, M. A. Hossain, *Polyhedron* **1984**, *3*, 95; M. M. A. Hossain, B. Hursthouse, A. I. M. Mazid, A. C. Sullivan, *J. Chem. Soc., Dalton Trans.* **1989**, 2347.

[9] R. R. Holmes, *Progr. Inorg. Chem.* **1984**, *32*, 119; M. C. Favas, D. L. Kepert, *ibid.* **1980**, *27*, 325; A. R. Rossi, R. Hoffmann, *J. Am. Chem. Soc.* **1975**, *14*, 365.

[10] [10a] K. Watenpaugh, C. N. Caughlan, *Inorg. Chem.* **1966**, *5*, 1782. – [10b] H. Haase, H. Hoppe, *Acta Crystallogr., Sect. B*, **1970**, *26*, 744. – [10c] G. W. Svetich, A. A. Voge, *J. Chem. Soc., Chem. Commun.* **1971**, 676. – [10d] R. Toth, D. W. Stephan, *Can. J. Chem.* **1991**, *69*, 172.

[11] H. Sugahara, Y. Shuto, *J. Organomet. Chem.* **1970**, *24*, 709.

[12] [12a] T. J. Boyle, N. W. Eilerts, J. A. Heppert, F. Takusagawa, *Organometallics* **1994**, *13*, 2218. – [12b] T. J. Boyle, D. L. Barnes, J. A. Heppert, L. Morales, F. Takusagawa, *Organometallics* **1992**, *11*, 1112.

[13] [13a] H. Yasuda, Y. Nakayama, K. Takei, A. Nakamura, Y. Kai, N. Kanehisa, *J. Organomet. Chem.* **1994**, *473*, 105. – [13b] S. L. Latesky, J. Keddington, A. K. McMullen, I. P. Rothwell, J. C. Huffman, *Inorg. Chem.* **1985**, *24*, 995.

[14] R. N. Renaud, J. W. Bovenkamp, R. D. Fraser, J.-L. A. Roustan, *Can. J. Chem.* **1977**, *55*, 3456.

[15] T. K. Prakasha, R. O. Day, R. R. Holmes, *Inorg. Chem.* **1992**, *31*, 726.

[16] [16a] G. M. Sheldrick, *SHELXS-86, Program for the Solution of Crystal Structures*, University of Göttingen, Germany, **1986**. – [16b] *SHELXL-93, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1993**.

[17] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-401400, the names of the authors and the journal citation.

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