Trigonal-Prismatic versus Octahedral Molecular Structures in $[(CH_3)_nMX_{6-n}]$ Compounds

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Abstract: The molecular structures of $[(CH_3)_5MoOCH_3]$, $[(CH_3)_4Mo(OCH_3)_2]$, $[(CH_3)_5WCl]$, and $[(CH_3)_3WCl(OCH_3)_2]$ are reported. The first three structures are based on trigonal-prismatic geometry, the last one on octahedral geometry.

Keywords: methyl complexes · molybdenum · structure elucidation · tungsten

Introduction

The preparations of the neutral hexacoordinate permethyl complexes $[W(CH_3)_6]$[1] and $[Re(CH_3)_6]$[2] have been followed by those of $[Mo(CH_3)_6]$,[3] as well as $[Zr(CH_3)_6]^{2-}$,[4] $[Nb(CH_3)_6]^-$,[5] and $[Ta(CH_3)_6]^-$.[5] In 1986 it had been predicted that these complexes should be nonoctahedral,[6] and the first experimental observation supporting this was the crystal structure of $[Zr(CH_3)_6]^{2-}$. Subsequently a number of theoretical calculations were all consistent with fact that MH_6 and $[M(CH_3)_6]$ (M = transition metal d^0, d^1, and d^2) should not be octahedral.[7–13] In the meantime the gas-phase structure of $[W(CH_3)_6]$ has been determined by electron diffraction,[14] and all the above-mentioned neutral or anionic hexamethyl compounds have now structurally characterized by single-crystal structure determinations.[3, 4, 15] The results can be summed up as follows: Neutral d^0 complexes such as $[W(CH_3)_6]$ and $[Mo(CH_3)_6]$ have a C_{3v} distorted trigonal-prismatic structure; the structure of $[Mo(CH_3)_6]$ is slightly more distorted than that of $[W(CH_3)_6]$. Anionic d^0 complexes have fairly regular trigonal-prismatic structures. Only $[Nb(CH_3)_6]^-$ possibly shows a very small trigonal distortion. d^1-$[Re(CH_3)_6]$ also has essentially a regular trigonal-prismatic structure. Interestingly, even these subtle differences have been predicted or reproduced by a thorough theoretical investigation.[13] The chemist is always in search of a simple explanation, and here too such a "rule of thumb" can be applied.[14] Under the reasonable assumption that no p orbitals of the metal atoms are involved in the metal–ligand bonding (or that p orbital participation is very small, as indeed is shown by calculations), the resulting sd^5 hybridisation of all *gerade* orbitals cannot lead to an octahedral or even regular trigonal-prismatic structure for group symmetry reasons.[16] More quantitatively, Pauling's valence bond model gives preference for predominant bond angles of 63° and 117° (180° – 63°).[7]

There are several structures that can be constructed with these angles, a strongly C_{3v} distorted trigonal-prismatic structure seems to be the chemically most reasonable one. The strong distortion of the trigonal prism will be diminished by repulsion forces between the larger methyl ligands, and can be reduced to zero if negative partial charges on the ligands increase the interligand repulsion further, as found in $[Ta(CH_3)_6]^-$ and $[Zr(CH_3)_6]^{2-}$. The stronger distortion of $[Mo(CH_3)_6]$ and $[Nb(CH_3)_6]^-$ in comparison to $[W(CH_3)_6]$ and $[Ta(CH_3)_6]^-$, respectively, is explained in terms of the onset of the relativistic effect in the latter cases which "normalizes" the bonding situation.[13] On the other hand, only one d electron as in $[Re(CH_3)_6]$ is also sufficient to reinstate the regular trigonal prism. A thorough discussion of these non-VSEPR structures and the influence of ligand repulsion, π-backbonding, and relativistic effects including a discussion of the often used models (extended VSPEPR model, electron core polarization, valence bond model, MO model) has been published recently.[17]

Of course all compounds such as WF_6, WCl_6, $[W(OR)_6]$, $[W(NR_2)_6]$, or their molybdenum analogues are assumed to be octahedral, and in many cases this has been confirmed experimentally.[18–22]

Here the question is addressed at what degree of substitution of $[(CH_3)_nMX_{6-n}]$ (M = Mo, W; X = F, Cl, OCH_3, $N(CH_3)_2$ etc) the trigonal prismatic/octahedral changeover occurs. Interesting dynamic behavior can be expected for borderline cases. For the system $[(CH_3)_nWCl_{6-n}]$ it has been calculated that the trigonal-prismatic structure will prevail for $n = 3-6$, while for $n \leq 2$ the octahedral structure predominates.[23] Previous attempts in the system $[(CH_3)_nWF_{6-n}]$ did not provide any conclusive results, due to the fact that in solutions of $[W(CH_3)_6]$ in WF_6 the mixed substituted compounds are present only in very small amounts, as evidenced by ^{19}F NMR

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spectroscopy.[5] [CH_3WCl_5] has already been prepared, but all attempts to obtain a molecular structure failed, since the crystals are inevitably disordered.[24] The theoretical prediction for its structure is that it is a slightly distorted octahedron of only C_s symmetry. Our search focuses on methyl-rich compounds. The transition from an octahedral to a prismatic structure is usually defined by a twist angle. In the cases presented below this discussion is not necessary since the found structures are very close to idealized trigonal-prismatic or octahedral ones.

Results and Discussion

[$(CH_3)_5MoOCH_3$] has been synthesized by two reactions [Eq. (1) and (2)]. In an attempt to recrystallize [$(CH_3)_5MoOCH_3$], [$(CH_3)_4Mo(OCH_3)_2$] has also been detected. It can be assumed that the formation of the latter is due to attack by molecular oxygen on [$(CH_3)_5MoOCH_3$] [Eq. (3)]. It has previously been shown that [$W(CH_3)_6$] ultimately will give [$W(OCH_3)_6$] if oxygen is carefully applied.[1] Unfortunately the isolation of [$(CH_3)_4Mo(OCH_3)_2$] was rather serendipitous and is probably due to very slow diffusion of atmospheric oxygen into the reaction vessel—conditions which are difficult to reproduce.

$$[MoOCl_4] + [Zn(CH_3)_2] \rightarrow [(CH_3)_5MoOCH_3] \qquad (1)$$

$$MoF_6 + Si(OCH_3)_4 \rightarrow [MoF_n(OCH_3)_{6-n}] \xrightarrow{[Zn(CH_3)_2]} [(CH_3)_5MoOCH_3] \qquad (2)$$

$$[(CH_3)_5MoOCH_3] \xrightarrow{O_2} [(CH_3)_4Mo(OCH_3)_2] \qquad (3)$$

[$(CH_3)_5WCl$] was prepared from WCl_6 and [$Zn(CH_3)_2$] [Eq. (4)], and similar to the previous reaction prolonged storage at low temperatures afforded small amounts of[$(CH_3)_3WCl(OCH_3)_2$].

$$WCl_6 \xrightarrow{[Zn(CH_3)_2]} [(CH_3)_5WCl] \xrightarrow{O_2,\ -90^{\circ}C} [(CH_3)_3WCl(OCH_3)_2] \qquad (4)$$

The structures of [$(CH_3)_5MoOCH_3$] and [$(CH_3)_5WCl$]: These two molecules have very similar structures, see Figure 1 and 2 and Table 1. The main conclusion is that upon substitution of one methyl group by an electron-rich ligand in [$Mo(CH_3)_6$] and [$W(CH_3)_6$] the structure clearly remains close to trigonal-prismatic.

Table 1. Bond lengths [pm] and selected bond angles [°] in [$(CH_3)_5MoOCH_3$] and [$(CH_3)_5WCl$].

	[$(CH_3)_5MoOCH_3$]		
Mo–O	184.6(1)	O-Mo-C4	97.13(7)
Mo–C1	217.3(2)	O-Mo-C2	96.50(7)
Mo–C2	212.8(2)	C2-Mo-C4	91.59(9)
Mo–C3	219.5(2)	C1-Mo-C3	74.88(9)
Mo–C4	212.7(1)	C1-Mo-C5	75.09(8)
Mo–C5	219.7(2)	C3-Mo-C5	77.74(10)
O–C	141.4(2)	Mo-O-C6	148.72(12)
	[$(CH_3)_5WCl$]		
W–Cl	232.9(2)	Cl-W-C1	90.0(1)
W–C1	219.1(4)	C1-W-C1′	92.4(2)
W–C2	217.8(5)	C2-W-C3	79.3(2)
W–C3	215.1(6)	C2-W-C2′	74.8(3)

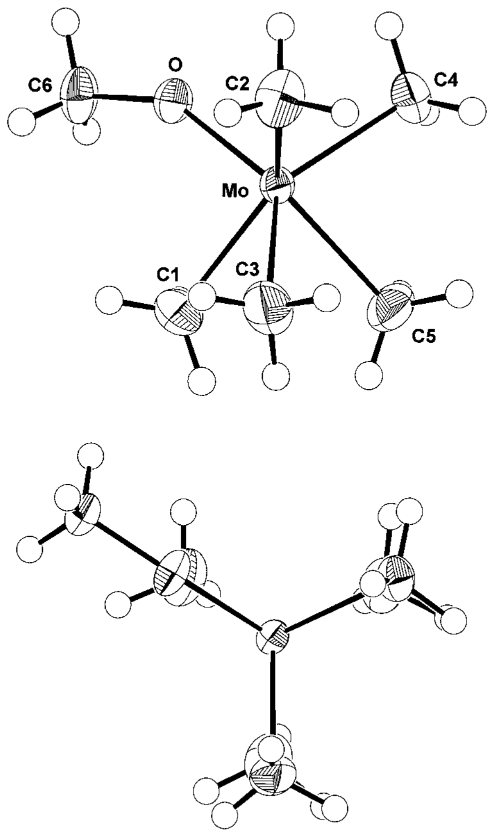


Figure 1. The molecular structure of [$(CH_3)_5MoOCH_3$] (ORTEP, 50% probability ellipsoids).

The influence of the electron-rich ligand is visible in that the bond angles in the hemisphere containing the electron-rich ligand increase to 90° and above. This can be understood in terms of increased repulsion between the ligands. Another view would be: Starting with the C_{3v}-distorted trigonal prism of [$Mo(CH_3)_6$] and [$W(CH_3)_6$] with three longer bonded methyl groups at an angle less than 80°, and three shorter bonded methyl groups, but at angles greater than 90°, the OCH_3 and Cl ligands occupy one position of the shorter bonded methyl groups with bond angles larger than 90°.

Indeed the methyl groups in the other hemisphere of the molecules remain at angles of less than 80° between each other, and in case of [$(CH_3)_5MoOCH_3$] these three Mo–C bond lengths remain longer than the other two. In [$(CH_3)_5WCl$] the opposite is observed for as yet unknown reasons. But in both cases the methyl group that eclipses the electron-rich ligand (if viewed along the threefold axis) has a shorter bond length to the central atom than the other two in the same hemisphere.

The structure of [$(CH_3)_4Mo(OCH_3)_2$]: As soon as one proceeds from the singly substituted to the doubly substituted compound, for example [$(CH_3)_4Mo(OCH_3)_2$], there are two positional isomers (*cis* and *trans*), if the structure is based on an octahedron, and three, if it based on a trigonal prism (see Scheme 1). The serendipitous mode of preparation and isolation of [$(CH_3)_4Mo(OCH_3)_2$] does not rule out the existence of other isomers than the one detected. But from Figure 3 and Table 2 it is evident that the structure

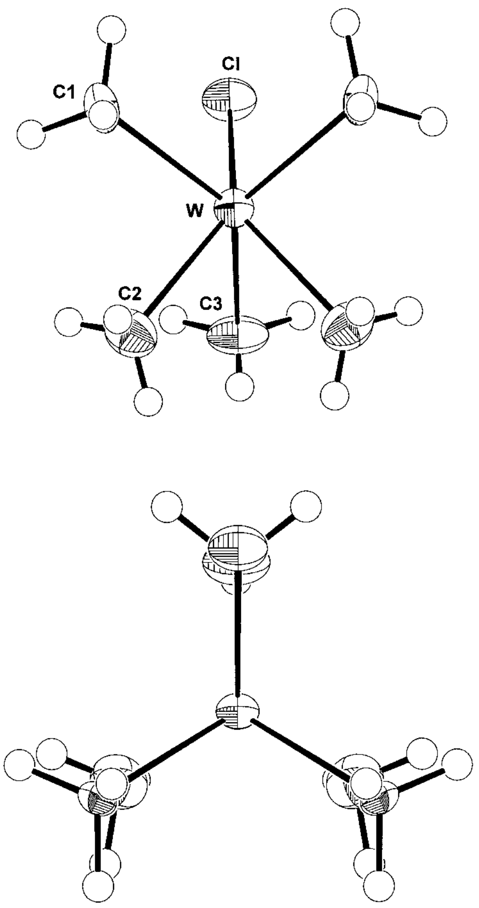
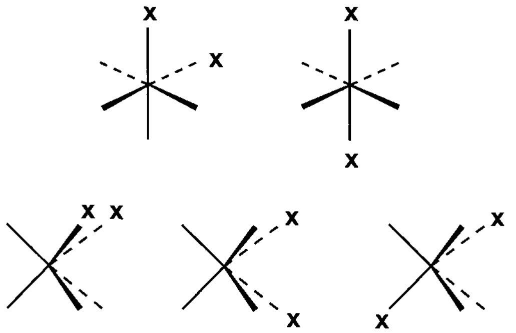


Figure 2. The molecular structure of $[(CH_3)_5WCl]$ (ORTEP, 50% probability ellipsoids). Unlabeled atoms are generated by the crystallographic mirror plane.



Scheme 1. Schematic representation of the two octahedral (top) and the three trigonal-prismatic MA_4X_2 isomers (bottom).

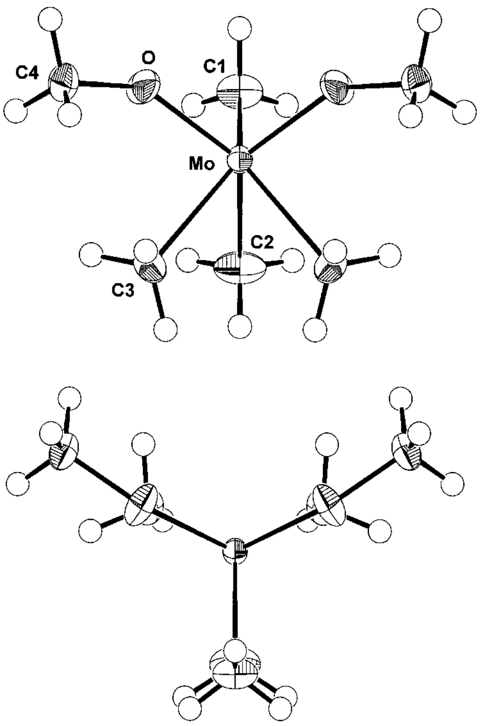


Figure 3. The molecular structure of $[(CH_3)_4Mo(OCH_3)_2]$ (ORTEP, 50% probability ellipsoids). Unlabeled atoms are generated by the crystallographic mirror plane.

Table 2. Bond lengths [pm] and selected bond lengths [°] of $[(CH_3)_4Mo(OCH_3)_2]$ and $[(CH_3)_3WCl(OCH_3)_2]$.

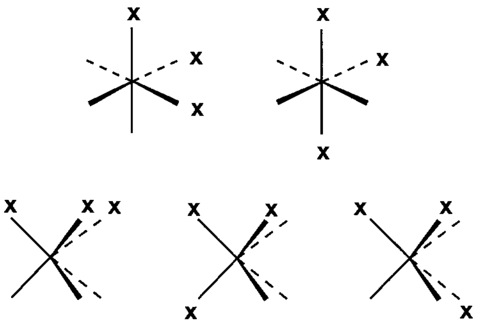
	$[(CH_3)_4Mo(OCH_3)_2]$		
Mo–O	185.9(2)	O-Mo-O′	99.67(1)
Mo–C1	213.4(4)	O-Mo-C1	91.8(1)
Mo–C2	219.9(4)	C2-Mo-C3	75.9(1)
Mo–C3	217.7(2)	C3-Mo-C3′	74.8(1)
C4–O	140.5(3)	Mo-O-C4	146.7(1)
	$[(CH_3)_3WCl(OCH_3)_2]$		
W–O1	180.9(3)	Cl-W-C5	166.6(2)
W–O2	182.3(3)	O1-W-O2	159.8(2)
W–Cl	248.9(1)	C3-W-C4	145.6(3)
W–C3	212.6(6)	Cl-W-O1	82.6(1)
W–C4	213.3(6)	Cl-W-O2	82.7(1)
W–C5	221.5(6)	Cl-W-C3	120.2(2)
O1–C1	141.2(6)	Cl-W-C4	94.0(2)
O2–C2	142.1(6)	O1-W-C4	89.1(2)
		O1-W-C4	94.5(2)
		O1-W-C5	101.9(2)
		O2-W-C3	89.1(2)
		O2-W-C4	100.2(2)
		O2-W-C5	95.6(2)
		C3-W-C5	73.0(2)
		C4-W-C5	73.2(3)

is still trigonal prismatic; both oxygen-carrying substituents occur in the same hemisphere of the molecule (see Scheme 1, bottom left). The angle between the two oxygen atoms has now increased to almost 100°, and the other two angles within the same hemisphere are also larger than 90°. The angles in the other hemisphere remain smaller than 80°, and these methyl groups have again, as in $[(CH_3)_5MoOCH_3]$, the larger Mo–C bond lengths. The similarities of the structures of $[(CH_3)_4Mo(OCH_3)_2]$ and $[(CH_3)_5MoOCH_3]$ can be taken as an indication that the observed structure of $[(CH_3)_4Mo(OCH_3)_2]$ is indeed the one of the most stable isomer.

The structure of $[(CH_3)_3WCl(OCH_3)_2]$: If we move to the third substitution of a methyl group by an electron-rich ligand, the following predictions can be made: In a trigonal-prismatic structure two isomers and in the case of the octahedral structure three isomers may be considered (see Scheme 2). Calculations have shown that $[(CH_3)_3WCl_3]$ should have a trigonal-prismatic structure with a substitution pattern as shown in Scheme 2, bottom right. This is the overall mini-

Table 3. Crystallographic data.

Compounds	$[(CH_3)_5MoOCH_3]$	$[(CH_3)_5WCl]$	$[(CH_3)_4Mo(OCH_3)_2]$	$[(CH_3)_4WCl(OCH_3)_2]$
M_r	202.14	294.47	218.14	326.47
T [°C]	– 80	– 100	– 153	– 153
space group	$P2_1/n$	$P2_1/m$	$P2_1/m$	$P\bar{1}$
a [pm]	667.74(4)	639.7(1)	626.6(1)	630.6(1)
b [pm]	1817.1(1)	1066.2(2)	1214.3(1)	765.5(1)
c [pm]	773.77(5)	675.1(1)	638.8(1)	999.8(2)
α [°]	90	90	90	80.42(1)
β [°]	107.646(1)	114.222(3)	108.95(1)	84.17(2)
γ [°]	90	90	90	80.06(1)
V [10^6 pm^3]	894.7(1)	419.9(1)	459.7(1)	467.4(1)
Z	4	2	2	2
μ [mm^{-1}] 1.39		13.98	1.37	12.58
θ_{max} [°]	30.5	30.6	24.9	34.95
reflections, collected	10562	1583	938	3584
reflections, independent	2737	1349	853	3448
refined parameters	147	54	75	128
R	0.018	0.023	0.017	0.034
$wR2$	0.041	0.052	0.042	0.092



Scheme 2. Schematic representation of the two octahedral (top) and the three MA_3X_3 isomers (bottom).

mum on the potential hypersurface.[21] The trigonal-prismatic isomer with all three chlorine atoms in one hemisphere (Scheme 2, bottom left) is calculated to be marginally less stable by 2.3 kJ mol^{-1}. The isomers based on octahedra appear only as transition states and are 26 kJ mol^{-1} higher (*mer* isomer) and 61.2 kJ mol^{-1} (*fac* isomer) less stable than the overall minimum (see Scheme 2.

The structure of the related $[(CH_3)_3WCl(OCH_3)_2]$ compound does not follow these predictions. It turns out that the $[(CH_3)_3WCl(OCH_3)_2]$ compound has an octahedral structure with meridial substitution (Figure 4). The W–C bond length *trans* to Cl is much longer than the other two. The overall structure resembles very much those calculated for the *mer*-$[(CH_3)_3WCl_3]$ transition state, including the small deviations from the ideal 90° and 180° angles. There may be two reasons for this serious discrepancy: As in case of the double substitution it cannot be assured that the reaction mixture does not contain other isomers. If, however, the observed structure represents the energy minimum for the compound, which we presume, then one can conclude that the OCH_3 ligands are better π donors than the Cl ligand, so that the octahedral symmetry is observed already in this case.

Conclusion

The trigonal-prismatic structure is retained for hexacoordinate neutral complexes when only one of the ligands has π-donor abilities, and the five others are σ-bonded only. This is probably correct also for the case of two π-donor ligands and four solely σ-bound ligands. The case reported here for three π-donor ligands and three solely σ-bound ligands indicates that the octahedron start to dominate as the structural principle at this point.

Experimental Section

All experiments were carried out under pure, dry argon. Compounds stable at room temperature were handled in a glove box (concentration of O_2 and H_2O < < 1 ppm). Solvents were dried over sodium and degassed. MoF_6 was obtained from Merck Co. (Darmstadt, Germany). WCl_6 was made by chlorination of W metal at 600 °C.[25] $MoOCl_4$ was purchased from Aldrich Inorganics. $[Zn(CH_3)_2]$ (1M solution in heptane) was purchased from Aldrich Inorganics, and $Si(OCH_3)_4$ from Fluka chemicals, Germany.

$[(CH_3)_5MoOCH_3]$: MoF_6 (360 mg, 1.72 mmol) and $Si(OCH_3)_4$ (1.04 g, 6.86 mmol) were condensed under vacuum into a 100 mL glass vessel at – 196 °C. After warming to room temperature, the mixture was stirred for 25 min. The solution turned yellow-brown. All volatile material was pumped off in vacuum for about 1 h. The remaining solid was dissolved in diethyl ether. At – 60 °C $[Zn(CH_3)_2]$ (190 mg, 1.99 mmol) was condensed

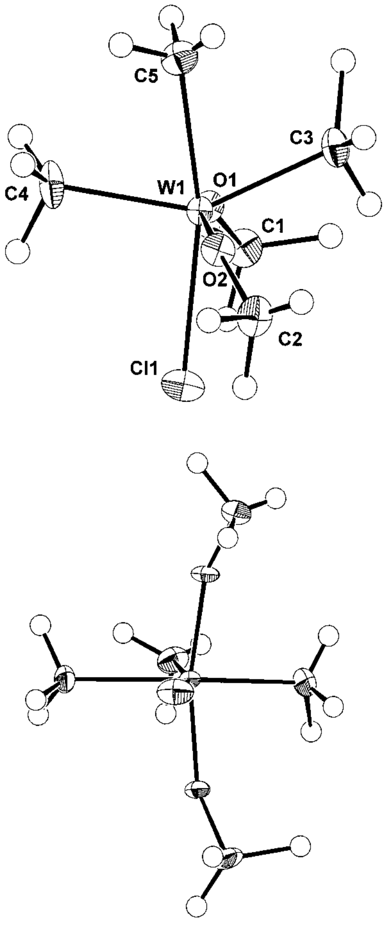


Figure 4. The molecular structure of $[(CH_3)_3WCl(OCH_3)_2]$ (ORTEP, 50% probability ellipsoids).

into the vessel, and the color changed to orange. After the mixture had been stirred for 30 min at -60 to $-50\,^\circ$C, the bulk of the diethyl ether was pumped off. The remaining solid was condensed from 36 °C into a $-196\,^\circ$C cold glass ampule. The residual diethyl ether was pumped off, and *n*-pentane was added. Upon cooling from $-50\,^\circ$C to $-90\,^\circ$C orange crystals were formed.

[(CH$_3$)$_5$MoOCH$_3$] from MoOCl$_4$: [MoOCl$_4$] (284 mg, 1.12 mol) was dissolved in Et$_2$O (15 mL) at $-78\,^\circ$C, the color of this solution was bordeaux red. [Zn(CH$_3$)$_2$] (230 mg, 2.41) was condensed on to the solution. A black precipitate was formed at $-77\,^\circ$C, and the solution turned orange brown. The mixture was stirred for 60 min at $-78\,^\circ$C, warmed over 10 min to $-10\,^\circ$C, kept at that temperature for 5 min, cooled to $-78\,^\circ$C, Et$_2$O was pumped off and the remaining solid was dissolved in *n*-pentane at $-78\,^\circ$C. This solution was quickly warmed to $-15\,^\circ$C and all solvents were pumped off at this temperature. The last fraction of this vacuum condensation contained [(CH$_3$)$_3$MoOCH$_3$] dissolved in *n*-pentane as a yellow substance. Residual pentane was pumped off slowly at $-78\,^\circ$C. The solid was dissolved in CF$_3$CH$_2$CF$_3$, and recrystallization from $-40\,^\circ$C to $-72\,^\circ$C afforded orange needles of [(CH$_3$)$_5$MoOCH$_3$].

A suitable crystal was isolated from the liquid by using a special device, cut to an appropriate size, and mounted on the needle tip of the goniometer head. All this was done while maintaining the temperature below $-100\,^\circ$C and under protection from air and water by nitrogen.[26] The goniometer head was mounted on a precooled Bruker SMART CCD 1000 TM diffractometer (Mo$_{K\alpha}$ radiation, $\lambda = 71.069$ pm, graphite monochromator, a distance of 0.3°in ω between frames, 10 s/frame, detector–crystal distance 4.0 cm). A full shell of data was measured by 1800 frames. Data were reduced to intensities, corrected for background, and an semiempirical absorption corrected was applied (SAINT and SADABS, as implemented in the measuring routine of the diffractometer). The structure was solved[27] and refined[28] by using the SHELXL procedures. All atoms except hydrogen were refined anisotropically, hydrogen atoms were refined isotropically. For further experimental detail of the structure, see Table 1.

[(CH$_3$)$_4$Mo(OCH$_3$)$_2$]: In one reaction of [MoOCl$_4$] and [Zn(CH$_3$)$_2$] spherical, yellow single crystals of [(CH$_3$)$_4$Mo(OCH$_3$)$_2$] were obtained, besides the bulk of orange needles of [(CH$_3$)$_5$MoOCH$_3$]. A suitable single crystal was mounted on an Enraf Nonius CAD 4 four-circle diffractometer with a self-made nitrogen-flow cooling system (Mo$_{K\alpha}$ radiation, $\lambda = 71.069$ pm, graphite monochromator). Cell constants were refined by fine setting of 25 reflections with $20^\circ << \theta << 25^\circ$. Reflections were measured by the ω scan mode, with 60 s per reflection, allowing 25 % of the time for background measurements. By applying Lorentz polarization and background correction, the data were reduced to intensities. A psi scan was applied by measuring eight reflections with $\chi >> 80^\circ$ in 37 steps of ψ from 0° to 380°. Structures were solved and refined by using the Shelx procedures.[27, 28] All atoms except hydrogen were refined anisotropically, hydrogen atoms were refined isotropically with one common isotropic displacement factor for all hydrogen atoms.

[(CH$_3$)$_5$WCl]: WCl$_6$ (323 mg, 0.79 mmol) was dissolved at $-78\,^\circ$C in Et$_2$O (20 mL), and [Zn(CH$_3$)$_2$] (110 mg, 1.15 mmol) was added at $-78\,^\circ$C. The mixture was stirred for 3 h at this temperature, then warmed to $-35\,^\circ$C. After the mixture had been stirred for 30 min, the color changed from black-green to red-brown. Et$_2$O was pumped off at this temperature, and *n*-pentane was condensed on to the solid. The orange-brown solution was transferred through a Teflon tube (inner diameter 1 mm) into a 8 mm glass ampule, while undissolved material remained. At $-50\,^\circ$C the bulk of the solvent was pumped off, and recrystallization from $-55\,^\circ$C to $-90\,^\circ$C afforded platelike crystals. **Caution**: [(CH$_3$)$_5$WCl] explodes at room temperature, and also on contact with oxygen. It can be sublimed at $-20\,^\circ$C. Preparation was also achieved in CH$_2$Cl$_2$, crystallization is best done with *n*-pentane. A suitable single crystal was measured as described for [(CH$_3$)$_5$MoOCH$_3$].

[(CH$_3$)$_3$WCl(OCH$_3$)$_2$]: A similar procedure to that described for [(CH$_3$)$_5$WCl] afforded a small amount of yellow crystals, if the final solution in *n*-pentane was kept at $-90\,^\circ$C for three weeks. A suitable single crystal was measured as described for [(CH$_3$)$_4$Mo(OCH$_3$)$_2$].

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-156645 ([(CH$_3$)$_5$MoOCH$_3$]), CCDC-156646 ([(CH$_3$)$_4$Mo(OCH$_3$)$_2$]), CCDC-156647 ([(CH$_3$)$_5$WCl]), and CCDC-156648 ([(CH$_3$)WCl(OCH$_3$)$_2$]). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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