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Facile Access to Homo- and Heteroleptic, Triply Bonded Dimolybdenum Hexaalkoxides with Unsaturated Alkoxide Ligands

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A series of monodentate, triply bonded $Mo_2(OR)_6$ complexes [R = MBE (**1**) (MBE = 2-methylbut-3-ene-2-yl), MMP (**2**) (MMP = 1-methoxy-2-methylpropane-2-yl), Terp (**3**) [Terp = 2-(4-methylcyclohex-3-enyl)propane-2-yl], which exhibit C–C double bonds or an ether function in the ligand sphere, were synthesized and characterized by multinuclear (^{1}H, ^{13}C and ^{95}Mo) NMR studies. The partial alcoholysis of the latter complexes with neopentyl alcohol (neopentOH) led to the heteroleptic alkoxides $Mo_2(OR)_n(Oneopent)_{6-n}$ (**4**–**7**) {n = 2 [for R = *t*Bu (**4**), MBE (**5**), MMP (**6**)], 4 [for R = Terp (**7**)]}. This concept was further applied to the synthesis of $Mo_2(O_2DMH)_2$-$(O$*t*$Bu)_2$ (**8**) (DMH = 2,5 dimethylhexyl) by starting from the $Mo_2(O$*t*$Bu)_6$ precursor. The ^{1}H NMR spectra for the heteroleptic complexes **4**–**8** show signals that are significantly shifted to a higher field for the RO ligand protons compared to those of their homoleptic analogues. This is the result of a change in the spatial position of the alkoxide ligands (RO) in the homoleptic compared to the heteroleptic complexes that leads to a different magnetic environment for the alkoxide ligands due to the magnetic anisotropy of the Mo–Mo triple bond. ^{95}Mo NMR studies of the complexes **1**–**8** show that the resonance strongly depends on the substitution pattern of the alkoxide and that a shift to higher field is observed when going from the tertiary to the primary alkoxides. The molecular structures for **4**–**8** were determined by single-crystal X-ray diffraction, and all of the complexes show a staggered conformation as well as an asymmetric ligand distribution, which results in unequal Mo–O bond lengths. For the heteroleptic complexes **4**–**7**, the RO ligands (R = *t*Bu, MBE, MMP and Terp, respectively) exhibit the longest bond lengths, which suggests that the position of the ligand strongly depends on the steric congestion of the α-carbon atom of the alkoxide ligand. In **6**, the methoxy function enables an intramolecular O→Mo coordination as is indicated by a Mo–O distance of 2.2464(7) Å. This fact is supported by a lengthening of the Mo–Mo triple bond.

Introduction

The first complex with a metal–metal multiple bond, $K_2[Re_2Cl_8]\cdot H_2O$, was described by Cotton et al. in 1965.[1] This discovery stimulated an increased interest in synthesizing other multiply bonded metal–metal complexes and has led to numerous well-defined systems with various metals.[2] Among these systems, the dinuclear, triply bonded Mo^{III} compounds of the type Mo_2R_6 (R = organyl) represent a fascinating group.[3] The synthesis of the first example, $Mo_2(CH_2SiMe_3)_6$, as described by Wilkinson et al.,[4] was extended by the seminal studies of Chisholm et al. on various systems with alkyl, dialkylamino[5] and alkoxido ligands at the molybdenum atoms.[6] The latter type of complexes, i.e. dimolydenum(III) hexaalkoxides, show an intriguingly versatile reactivity that included the addition of Lewis bases,[7] oxidative addition reactions,[8,9] the addition of alkynes,[10,11] CO_2 insertion[12] and the reversible addition of CO.[13,14] Furthermore, these complexes display interesting structural features, i.e. an asymmetric ligand distribution that resulted in different Mo–O bond lengths in the same molecule,[15] that are not yet fully understood. Their structural characterization can be difficult[15,16] due to the disorder of the Mo_2 entity.[17] In addition, the heteroleptic, triply bonded dimolybdenum complexes of the structure $Mo_2A_2B_4$ are known[18] and prefer the conformation **b** with both ligands equally distributed at the Mo atoms (Figure 1). A high kinetic barrier between the conformers **a** and **b** prevents transmutational processes.

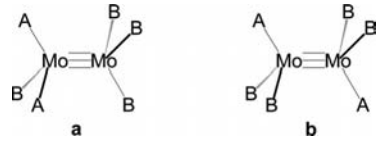

Figure 1. Possible configurations for the heteroleptic $Mo_2A_2B_4$ complexes. A and B can be various ligands, e.g., amido, halogenido, alkyl, alkoxido, etc.

Various $Mo_2A_2B_4$ complexes with different ligands A and B (e.g., amido, halogenido and alkyl) have been described and have even been employed for the synthesis of unique heterodimetallic clusters.[19] Unexpectedly, heteroleptic complexes that contain only alkoxido ligands and homoleptic complexes with unsaturated alkoxido ligands are currently unknown. This prompted us to introduce dif-

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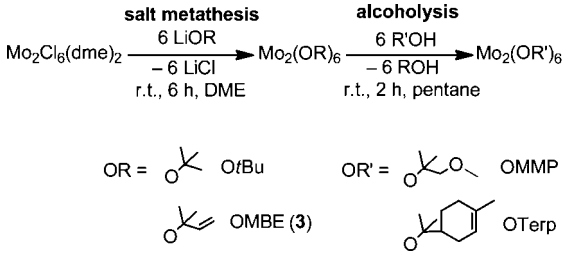
ferent alkoxide groups at the triply bonded Mo–Mo system. These alkoxide groups bear additional functionalities that could be useful for subsequent modifications such as immobilization on supports and self-assembly.

Results and Discussion

Syntheses

Homoleptic $Mo_2(OR)_6$ (1–3) (R = MMP, Terp and MBE)

We chose to introduce the functional alcohols MBEOH (MBE = 2-methylbut-3-ene-2-yl), MMPOH (MMP = 1-methoxy-2-methylpropane-2-yl) and TerpOH [Terp = 2-(4-methylcyclohex-3-enyl)propane-2-yl], which possess either a C–C double bond or a methoxy group, to the dimolybdenum triple bond by direct alcoholysis of the precursor $Mo_2(OtBu)_6$.[15] Tertiary alcohols were employed exclusively due to their steric congestion in order to prevent intermolecular oligomerization to $[Mo(OR)_3]_x$. Complexes $Mo_2(OMMP)_6$ (**1**) and $Mo_2(OTerp)_6$ (**2**) were obtained as orange powders after the addition of an excess of the corresponding alcohol at room temperature to a pentane solution of $Mo_2(OtBu)_6$[20] (Scheme 1) in 74% and 67% yield, respectively. Unfortunately, the addition of MBEOH under the same conditions afforded only a mixture of products. However, the reaction of $Mo_2Cl_6(DME)_2$ with in situ generated LiOMBE in DME yielded the desired complex $Mo_2(OMBE)_6$ (**3**) in 79% yield.[20]

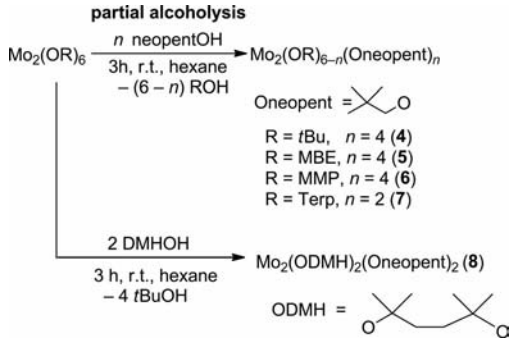


Scheme 1. Synthesis of functionalized $Mo_2(OR)_6$ complexes **1**–**3**.

To the best of our knowledge, no transition metal complex bearing the (–)-*p*-terpineolate ligand has been reported to date. The metathesis and alcoholysis reactions led to almost pure products (^{1}H NMR) that were purified by means of recrystallization. Complexes **1** and **3** were also isolated by sublimation (100–120 °C, 10^{-3} mbar), whereas complex **2** decomposed under these conditions without subliming.

Heteroleptic $Mo_2(OR)_n(Oneopent)_{6-n}$ (4–7) [R = tBu, MBE, MMP (n = 2), Terp (n = 4)] and $Mo_2(ODMH)_2(OtBu)_2$ (8)

In addition, we probed the suitability of $Mo_2(OtBu)_6$ as a precursor to the heteroleptic, triply bonded dimolybdenum alkoxides through partial alkoxido ligand exchange. Thus, we probed the reactivity of monodentate neopentOH (neopentOH = neopentyl alcohol) and bidentate DMHOH (DMH = 2,5 dimethylhexyl) towards $Mo_2(OtBu)_6$ in a hexane solution in a molar ratio of 4:1 and 2:1, respectively. In both cases we obtained the desired heteroleptic derivatives $Mo_2(OtBu)_2(Oneopent)_4$ (**4**) and $Mo_2(OtBu)_2(ODMH)_2$ (**8**) (Scheme 2) in 65% and 89% yield, respectively. When a smaller molar ratio of the alcohol was used, **4** and **8** were formed, and $Mo_2(OtBu)_6$ remained; but when an excess of the alcohol was used, the respective homoleptic analogues were formed. Furthermore, we applied the same protocol for the synthesis of heteroleptic and additionally functionalized alkoxide compounds, starting from the precursors **1**–**3**. The conversion of **1** and **3** with neopentOH in a molar ratio of 1:4 afforded the desired complexes $Mo_2(OMBE)_2(Oneopent)_4$ (**5**) and $Mo_2(OMMP)_2(Oneopent)_4$ (**6**) in 89% and 76% yield, respectively. However, the partial alcoholysis of complex **2** in a molar ratio of 1:4 did not result in the replacement of the four TerpO ligands, but led to complex $Mo_2(OTerp)_4(Oneopent)_2$ (**7**) in 85% yield (Scheme 2), as proven by ^{1}H NMR spectroscopy. Interestingly, when an excess of neopentOH was used in the reactions with **1**–**3**, complete alkoxido exchange did not occur to give the homoleptic analogue $Mo_2(Oneopent)_6$. Instead, a mixture of products with varying ligand distributions was observed. The new complexes **4**–**8** were isolated as yellow, crystalline solids by means of recrystallization or sublimation (100–120 °C, 10^{-3} mbar).



Scheme 2. Partial alcoholysis of $Mo_2(OtBu)_6$ and complexes **1**–**3** with neopentOH to afford the heteroleptic complexes **4**–**7**, as well as the partial alcoholysis of $Mo_2(OtBu)_6$ with DMHOH to afford the heteroleptic complex **8**.

NMR Studies

Complexes **1**–**8** were characterized by ^{1}H, ^{13}C and ^{95}Mo NMR spectroscopy. In the ^{1}H NMR spectra the peaks assigned to the alkoxido ligand protons for the homoleptic complexes **1**–**3** are significantly shifted to a lower field compared to the signals of the corresponding alcohols and lithium alcoholates, respectively, which confirms the successful coordination of the ligands to the Mo_2 entity (Table 1).[2] The signal shift in the ^{1}H NMR spectra for compound **1** and its corresponding lithium alcoholate is exemplified in Figure 2.

Table 1. Selected ^{1}H and ^{13}C NMR data for **1**–**8**; δ values in ppm; R represents the respective alcohol.

	^{1}H NMR[a]	^{13}C NMR
1[a]	3.44 ($R_2CH_2OCH_3$)	81.7 (R_3CO)
	3.18 ($R_2CH_2OCH_3$)	78.9 ($R_2CH_2OCH_3$)
	1.60 (RCH_3)	58.2 ($R_2CH_2OCH_3$)
		29.0 (RCH_3)
2[a]	5.53 ($R_2C=CHR$)	133.6 ($R_2C=CHR$)
	1.70 (RCH_3)	121.8 ($R_2C=CHR$)
	2.47–1.46[b]	83.6 ($R_3C–O$)
	1.25 ($R–CH_3$)	47.0, 31.7, 29.6, 25.7, 23.8, 23.1[b]
3[a]	6.26 ($RHC=CH_2$)	147.6 ($RHC=CH_2$)
	5.24 ($RHC=CH_2$)	111.0 ($RHC=CH_2$)
	4.93 ($RHC=CH_2$)	81.2 (R_3CO)
	1.62 (RCH_3)	28.8 (RCH_3)
4[a]	1.17 (RCH_3)	88.62 (R_3CO)
	5.25 (OCH_2R)	34.27 ($RCCH_3$)
	1.13 (RCH_3)	76.67 (OCH_2R)
		32.22 (R_3CCH_2O)
		26.36 (RCH_3)
5[a]	5.70 ($RHC=CH_2$)	146.8 ($RHC=CH_2$)
	4.92 ($RHC=CH_2$)	110.1 ($RHC=CH_2$)
	4.66 ($RHC=CH_2$)	80.5 (R_3CO)
	1.62 (RCH_3)	28.0 (RCH_3)
	5.32 (OCH_2R)	80.5 (OCH_2R)
	1.07 (RCH_3)	34.7 (R_3CCH_2O)
		28.0 (RCH_3)
6[a]	2.68 (RCH_2OCH_3)	87.9 (R_3CO)
	2.55 (RCH_2OCH_3)	80.5 (RCH_2OCH_3)
	1.33 (RCH_3)	57.4 (RCH_2OCH_3)
	5.38 (OCH_2R)	26.5 (RCH_3)
	1.20 (RCH_3)	77.9 (OCH_2R)
		34.3 (R_3CCH_2O)
		27.6 (RCH_3)
7[a]	5.31 ($R_2C=CHR$)	133.2 ($R_2C=CHR$)
	1.61 (RCH_3)	121.2 ($R_2C=CHR$)
	2.14–1.26[b]	83.5 (R_3CO)
	1.19 (RCH_3)	46.4, 34.4, 29.2, 26.3, 24.4, 23.2[b]
	5.52 (OCH_2R)	77.3 (OCH_2R)
	1.17 (RCH_3)	31.3 (R_3CH_2O)
		27.5 (RCH_3)
8[c]	1.77 (RCH_2R)	82.4 (R_3CO)
	1.27 (RCH_2R)	37.6 (RCH_2R)
	1.11 (RCH_3)	32.4 (RCH_2R)
		27.6 (RCH_3)
		68.2 (R_3CO)
		31.3 (RCH_3)

[a] The chemical shifts were measured in [D_6]benzene at 25 °C. [b] The respective resonances overlapped and could not be assigned unambiguously. [c] The chemical shifts were measured in [D_1]-chloroform at 25 °C.

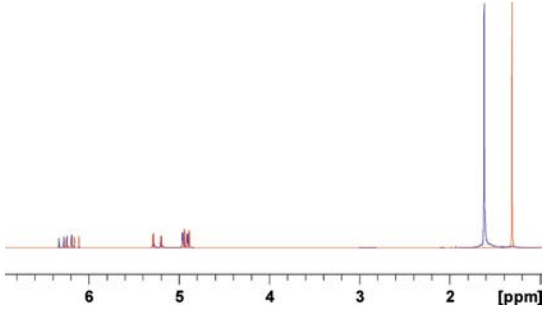


Figure 2. Comparison between the ^{1}H NMR spectra for **1** (blue) and its corresponding lithium alcoholate (red).

For the heteroleptic complexes **4**–**8**, we observed the resonances that corresponded to both of the alkoxido ligands in the expected integral ratios (Table 1).

However, when comparing the signals of the homoleptic complexes **1**–**3** with the signals of the corresponding heteroleptic analogues **4**–**7**, we observed an interesting phenomenon. In the ^{1}H NMR spectra for the complexes **4**–**7**, the resonances that correspond to the functional ligands (MMPO) are shifted to higher field, and the resonances that correspond to the neopent ligand are shifted to lower field; this is exemplified in Figure 3 by compound **6**. This effect can be explained by taking into account the diamagnetic anisotropy of the dimolybdenum triple bond.[2,21,22] In general, the protons that are closer to the axis of the Mo–Mo triple bond are more shielded, and the protons that are equatorial to it are more deshielded. This effect, which was originally proposed in 1972 by San Filippo,[23] was first observed by means of low-temperature NMR measurements for $Mo_2(NMe_2)_6$[5] and resulted in a splitting of the singlet signal observed at room temperature into two different resonances for the magnetically nonequivalent methyl groups. In the present case we assume that the different resonances are a result of a change in the spatial position of the attached ligands relative to the Mo–Mo triple bond on going from the homoleptic to the heteroleptic complexes, which is due to the change in the geometric environment caused by the different adjacent ligands.

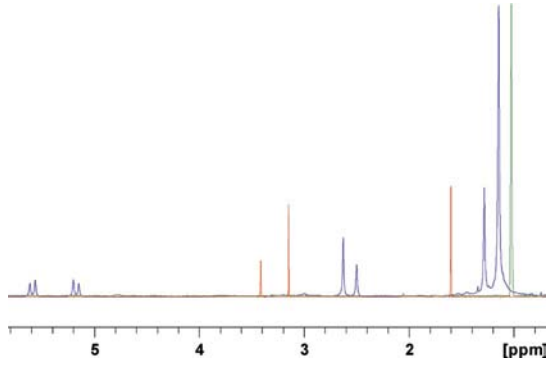


Figure 3. Comparison between the ^{1}H NMR spectra for **6** (blue), its corresponding homoleptic derivative **3** (red) and $Mo_2(Oneopent)_6$ (green). The spectra were measured in [D_6]benzene.

A similar effect was observed for complex **8**. Here, the expected set of signals was observed, but the resonance that corresponds to the ethylene bridge in the DMH ligand was strongly shifted to lower field. Once again we attributed this shift to the diamagnetic anisotropy of the Mo–Mo triple bond. If we assume, as previously reported, that the Mo–Mo triply bonded complexes are invariant to conformational changes in solution, we can approximately compare the crystallographic data with the obtained NMR chemical shifts (Figure 9). In complex **8**, the DMH ligand bridges the Mo–Mo triple bond, and the ethylene unit is located across the axial position. Owing to the aforementioned anisotropy, the related protons should be strongly deshielded. In fact, the corresponding ^{1}H NMR resonance appears at low field (δ = 1.77 ppm).

^{95}Mo NMR measurements for **1**–**8** were performed in order to confirm the presence of the Mo–Mo triple bond, which gives rise to significant resonances at lower field. This enabled us to easily distinguish the dimolybdenum(III) alkoxides from the mononuclear Mo^{III} species and the other species with Mo in different oxidation states (Figure 4).[24]

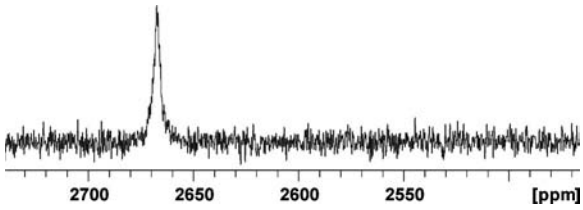


Figure 4. ^{95}Mo NMR spectrum for **1**, which was dissolved in [D_6]-benzene.

Although the resonances are relatively broad and low in intensity, which is due to the quadrupole moment and the relatively low natural abundance of the ^{95}Mo nuclei, we were able to confirm that the triple bond of the Mo_2 subunit is retained in solution (Table 2).

Table 2. ^{95}Mo NMR data for **1**–**8**.[a]

Compound	δ [ppm]	Compound	δ [ppm]
1	2632	**5**	2611
2	2720	**6**	2602
$Mo_2(OtBu)_6$[24]	2645	**7**	2481
3	2667	**8**	2689
4	2593	$Mo_2(neopent)_6$[24]	2445

[a] The chemical shifts were measured in [D_6]benzene at 25 °C.

As previously reported, the resonances depend on the substitution pattern at the Mo–Mo triple bond, and the shielding of the ^{95}Mo nuclei increases from the tertiary to the secondary and the primary alkoxides.[24] Interestingly, the synthesized heteroleptic complexes gave rise to resonances that are the average of those observed for the corresponding homoleptic derivatives.

Molecular Structures

Complexes **4**–**8** were investigated by single-crystal X-ray diffraction analysis (Table 4). In general the complexes show a typical "ethane-like" constitution and an asymmetric ligand distribution around the dimolybdenum triple bond (Figure 10), as reported for their homoleptic $M_2(OR)_6$ (M = Mo, W) analogues.

$Mo_2(OtBu)_2(Oneopent)_4$ (4)

The crystal structure of **4** (Figure 5) revealed an Mo–Mo bond length of 2.2217(8) Å, which is similar to the value reported for the homoleptic complex $Mo_2(Oneopent)_6$ [2.222(2) Å]. The alkoxido ligands are located in a staggered conformation and exhibit Mo–O bond lengths of 1.906(3), 1.896(3) and 1.883(3) Å.

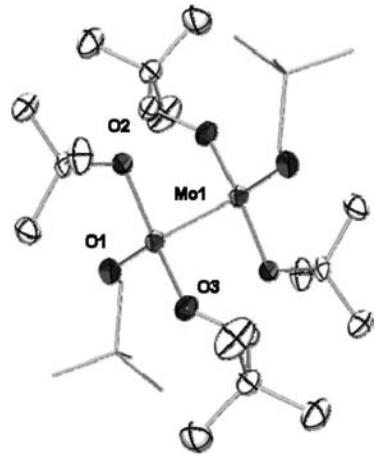


Figure 5. ORTEP presentation of the heteroleptic compound **4**. Hydrogen atoms and equal ligands are omitted for clarity.

The *t*BuO ligands exhibit the longest Mo–O bond [1.906(3) Å] in the molecular structure of **4**. They are connected to different molybdenum atoms and are thus *trans* to one another. In addition, they are oriented differently in space relative to the Mo–Mo triple bond compared to the neopentO ligands.

$Mo_2(OMBE)_2(Oneopent)_4$ (5)

The Mo–Mo bond length for complex **5** is 2.2219(14) Å, which is practically the same as that for **4** and for the related homoleptic analogues (Table 3).[24] As described for the *t*BuO ligands in **4**, the MBE ligands are located differently from the residual neopentO ligands relative to the Mo–Mo triple bond and display the longest Mo–O bond [1.920(4) Å] in the molecular structure of **5** (Figure 6).

Table 3. Selected bond lengths [Å] and angles [°] for **4**–**8**.

	4[a]	**5**[a]	**6**	**7**[a]	**8**[b]
Mo1–Mo1′	2.2217(8)	2.2219(14)	2.2416(11)	2.2464(7)	2.246(1)
Mo1–O2	1.906(3)	1.920(4)	1.929(5)	1.880(3)	1.887(4)
Mo1–O3	1.896(3)	1.879(4)	1.889(5)	1.912(3)	1.887(4)
Mo1–O1	1.883(3)	1.887(4)	1.901(4)	1.872(3)	1.924(6)
O1–Mo1–O2	114.45(14)	115.47(17)	115.7(2)	109.82(12)	115.8(2)
O2–Mo1–O3	115.89(14)	116.60(18)	118.1(2)	116.36(12)	111.4(2)
O3–Mo1–O1	115.44(14)	115.47(17)	114.7(2)	116.22(11)	115.8(2)

[a] The selected data corresponds to only one of the two molecules in a single unit cell. [b] O2 and O3 are identical due to the crystal symmetry in complex **8**.

Interestingly, the C–C double bond is turned towards the Lewis-acid site of the triple bond (average distance 3.416 Å), which could indicate π–metal interactions. However, no lengthening of the Mo–Mo triple bond is observed. Thus, this interaction appears to be very weak, and the orientation of the ligand may be induced by the crystal packing.

$Mo_2(OMMP)_2(Oneopent)_4$ (6)

In complex **6**, which was formally obtained by the exchange of the C–C double bond in complex **5** with a methoxy group, the Mo–Mo distance is significantly elongated

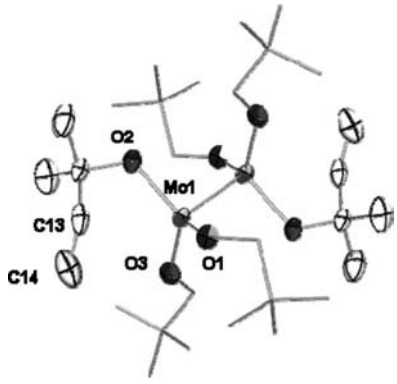


Figure 6. ORTEP presentation of the heteroleptic complex **5**. Hydrogen atoms and equal ligands are omitted for clarity.

to 2.2416(11) Å (Figure 7). Once again, the MMPO ligands exhibit the longest Mo–O bond [1.929(5) Å] in the molecular structure of **6**, and they are oriented differently in space from the neopentO ligands. Similarly to **5**, the oxygen atom of the methoxy functionality points towards the Lewis-acid site of the Mo–Mo triple bond, which led to a relatively short intramolecular O4→Mo distance of 2.665 Å and thus potential Mo–O interactions. This was further supported by the lengthening of the Mo–Mo distance for **6** (2.242 vs 2.221 Å in **5**).

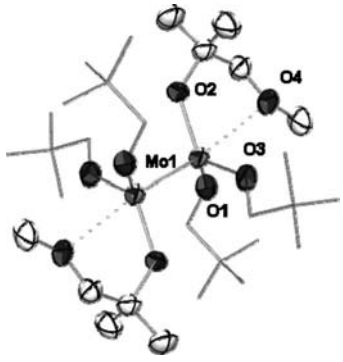


Figure 7. ORTEP presentation of the heteroleptic complex **6**. Hydrogen atoms and equal ligands are omitted for clarity.

$Mo_2(OTerp)_4(Oneopent)_2$ (7)

The crystal structure for **7** confirmed that only two, rather than four, of the TerpO ligands were exchanged by the partial alcoholysis of the $Mo_2(OtBu)_6$ precursor. The Mo–Mo bond [2.2464(7) Å] is significantly longer than those for complexes **4** and **5** (Figure 8), which is most likely because of the steric congestion of the TerpO ligands.

This complex shows unequal Mo–O bond lengths in a similar pattern to the other complexes described herein. The longest Mo–O bond [1.912(3) Å] in the molecular structure for **7** is exhibited by one pair of the TerpO ligands.

$Mo_2(ODMH)_2(OtBu)_2$ (8)

The Mo–Mo bond length for complex **8** is 2.246(1) Å (Figure 9). The slightly longer bond compared to those of the unfunctionalized monodentate analogues is most probably caused by the introduction of the bidentate ligand, as already reported for other complexes.[15] Once again, unequal Mo–O distances are observed. In this case, the *t*BuO ligands exhibit the longest Mo–O bond [1.924(6) Å] in the molecular structure of **8** and a different orientation relative to the dimolybdenum triple bond.

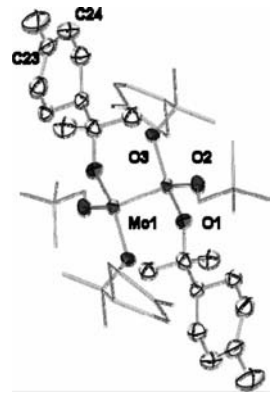


Figure 8. ORTEP presentation of the homoleptic complex **7**. Hydrogen atoms and equal ligands are omitted for clarity.

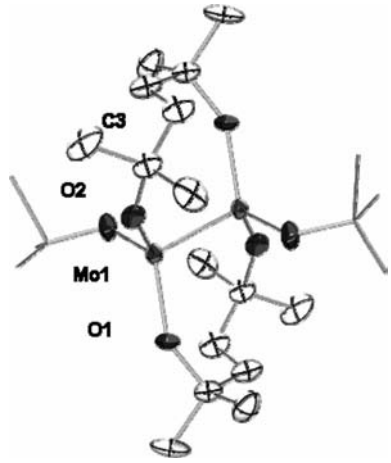
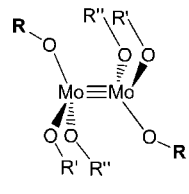


Figure 9. ORTEP presentation of the homoleptic complex **8**. Hydrogen atoms and equal ligands are omitted for clarity.

In Figure 10, the general pattern for the asymmetric distribution of the alkoxide ligands in the complexes **4**–**8** is diagrammed.



	R'	R''	R
4	neopent	neopent	*t*Bu
5	neopent	neopent	MBE
6	neopent	neopent	MMP
7	neopent	Terp	Terp
8	DMH/2	DMH/2	*t*Bu

Figure 10. Schematic presentation of the asymmetric ligand distribution in the heteroleptic alkoxides **4**–**8**.

In the heteroleptic complexes **4**–**7**, the tertiary alcohol always exhibits the differing ligand position (**R**), which has the longest Mo–O bond and exhibits the different orienta-

tion in the corresponding molecule. Although the reason for this favoured asymmetric distribution around the dimolybdenum triple bond is unknown, the data shows a clear correlation between the steric congestion of the α-carbon atom of the alkoxido ligand and the resulting distribution in the heteroleptic, monodentate complexes. Based on the literature and on our own observations,[2] we assumed that the main factor that determines the arrangement of the alkoxido ligands in the heteroleptic complexes is the provision of the best possible metal–metal interaction and thus a strong Mo–Mo triple bond. Owing to the different steric demand of the alkoxido ligands, the tertiary alkoxides prefer a distinct ligand position in order to minimize the intramolecular repulsion (Figure 10).

Conclusions

In this paper we have presented the successful introduction of different functional alkoxide groups into triply bonded Mo–Mo complexes. The alkoxides have a C–C double bond and a methoxy group in their ligand backbone. Furthermore, partial alcoholysis was applied in order to synthesize previously unknown heteroleptic, monodentate alkoxides. The resulting complexes **1**–**8** show that the ^{1}H NMR chemical shifts of the attached alkoxide ligands are substantially influenced by the magnetic anisotropy of the Mo–Mo triple bond. All of the new complexes were investigated structurally and reveal a general pattern in the distribution of the unequal Mo–O bond lengths. The new functionalized complexes could be useful building blocks for inorganic–organic hybrid polymers and/or for heterogenization of dimolybdenum complexes on solid supports. The investigations into the respective applications are currently in progress.

Experimental Section

General Methods and Starting Materials: All of the reactions were performed under anaerobic conditions by using standard Schlenk techniques. The solvents and alcohols were purchased from Sigma Aldrich, TCI Europe and Alfa Aesar, heated at reflux in the presence of an appropriate drying agent, distilled, degassed and N_2-saturated prior to use. The starting materials $Mo_2Cl_6(DME)_2$ and $Mo_2(OtBu)_6$[20] were synthesized as described in the literature with only slight variations.

Instrumentation and Physical Measurements: The ^{1}H and ^{13}C NMR spectra (TMS standard) were recorded with Bruker ARX 200 (^{1}H, 200 MHz; ^{13}C, 50 MHz) and ARX 400 (^{1}H, 400 MHz; ^{13}C, 100.64 MHz) spectrometers at ambient temperature. The ^{95}Mo NMR spectra (Na_2MoO_4 as standard) were recorded with a Bruker DRX 600 (^{95}Mo, 39.2 MHz) spectrometer, equipped with a 5 mm BBO probe head and ATM unit by using self-shielded gradients. The experiments were performed without proton decoupling and with a repetition rate of 4 scans per second, a 200 ms relaxation time and a 50 ms acquisition time. The elemental analyses were performed with a Perkin–Elmer Series II CHNS/O Analyzer 2400 instrument.

Single-Crystal X-ray Structure Determination: The single-crystals were mounted on a glass capillary in perfluorinated oil and measured in a cold stream of N_2. The data for **4**–**8** were collected with a Bruker-AXS SMART CCD diffractometer (Mo-K_α radiation, λ = 0.71707 Å, ω-scan). The structures were solved by direct methods. The refinements were carried out with the SHELXL-97 package.[25] All of the thermal displacement parameters were refined anistropically for non-H atoms and isotropically for H atoms. All of the refinements were carried out by full-matrix least-squares refinement on F^2. Details are listed in Table 4. CCDC-764328 (for **5**), -764329 (for **6**), -764330 (for **4**), -764331 (for **7**) and 783446 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

$Mo_2(OMMP)_6$ (1): A solution of MMPOH (416 mg, 4 mmol) in hexane (4 mL) was slowly added at room temperature to a solution of $Mo_2(OtBu)_6$ (400 mg, 0.64 mmol) in hexane (10 mL). The solution was stirred overnight, and an almost pure, orange solid was obtained after evaporation of the volatiles. The product was purified by recrystallization, using very small volumes of hexane, and obtained as an orange powder. The yield was 74% (384 mg, 0.47 mmol). $C_{30}H_{66}Mo_2O_{12}$ (810.7): calcd. C 44.44, H 8.21; found C 43.81, H 7.93. ^{1}H NMR (C_6D_6, 298 K): δ = 3.44 (s, 12 H), 3.18 (s, 18 H), 1.60 (s, 36 H) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 81.7 (s), 78.9 (s), 58.2 (s), 29.0 (s) ppm. ^{95}Mo NMR (C_6D_6, 298 K): δ = 2632 ppm.

$Mo_2(OTerp)_6$ (2): A solution of (–)-*p*-terpineol (308 mg, 2 mmol) in hexane (2 mL) was slowly added at 0 °C to a solution of $Mo_2(OtBu)_6$ (200 mg, 0.32 mmol) in hexane (5 mL). The solution was warmed to room temperature and stirred overnight. An almost pure, orange solid was obtained after evaporation of the volatiles. The product was purified by recrystallization, using very small volumes of hexane, and obtained as an orange, crystalline solid. The yield was 67% (234 mg, 0.21 mmol). $C_{60}H_{102}Mo_2O_6$ (1111.3): calcd. C 64.85, H 9.25; found C 64.53, H 9.18. ^{1}H NMR (C_6D_6, 298 K): δ = 5.53 (br. s, 6 H), 1.70 (br. s, 36 H), 1.46–2.47 (br. m, 7 H), 1.25 (br. s, 3 H) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 133.6 (s), 121.8 (s), 83.6 (s), 47.0 (s), 31.7 (s), 29.6 (s), 25.7 (s), 23.8 (s), 23.1 (s) ppm. ^{95}Mo NMR (C_6D_6, 298 K): δ = 2720 ppm.

$Mo_2(OMBE)_6$ (3): MBEOH (176 mg, 2.04 mmol) was dissolved in hexane (5 mL), and 1 equiv. of BuLi (1.3 mL of a 1.6 M hexane solution) was added at –78 °C. After the reaction mixture had been allowed to warm to room temperature, the volatiles were evaporated in vacuo. Hexane (5 mL) was added, followed by the slow addition of $Mo_2Cl_6(DME)_2$ (200 mg, 0.34 mmol) at –20 °C. After the solution had been stirred overnight, it was filtered through Celite, and the filter cake was washed with hexane (2 × 2 mL). The solvent was evaporated from the combined filtrates to give an orange-brown residue. This solid was extracted with hexane (2 × 5 mL), and the extracts were filtered to give a dark orange solution. Evaporation of the volatiles led to an orange, analytically pure solid. The yield was 79% (186 mg, 0.27 mmol). $C_{30}H_{54}Mo_2O_6$ (702.6): calcd. C 51.28, H 7.75; found C 50.74, H 7.71. ^{1}H NMR (C_6D_6, 298 K): δ = 6.26 (q, $^3J_{H,H}$ = 17.28 Hz, $^3J_{H,H}$ = 10.80 Hz, 6 H), 5.24 (dd, $^3J_{H,H}$ = 17.28 Hz, $^2J_{H,H}$ = 1.50 Hz, 12 H), 4.93 (dd, $^3J_{H,H}$ = 10.80 Hz, $^2J_{H,H}$ = 1.50 Hz, 1 H), 1.62 (s, 36 H) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 147.6 (s), 111.0 (s), 81.2 (s), 28.8 (s) ppm. ^{95}Mo NMR (C_6D_6): δ = 2667 ppm.

$Mo_2(OtBu)_2(Oneopent)_4$ (4): A solution of neopentOH (114 mg, 1.3 mmol) in hexane (2 mL) was added dropwise at room temperature to a solution of $Mo_2(OtBu)_6$ (200 mg, 0.32 mmol) in hexane (5 mL). After the solution had been stirred for 3 h, the volatiles were evaporated in vacuo, which resulted in a yellow solid. The

Table 4. Single-crystal X-ray data and refinement parameters for **4**–**8**.

	4	**5**	**6**	**7**	**8**
Empirical formula	$C_{28}H_{62}Mo_2O_6$	$C_{30}H_{62}Mo_2O_6$	$C_{30}H_{66}Mo_2O_8$	$C_{50}H_{90}Mo_2O_6$	$C_{24}H_{50}Mo_2O_6$
M [g/mol]	686.66	710.68	746.71	979.10	626.52
T [K]	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	triclinic	triclinic	triclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$Pnnm$
a [Å]	11.9298(3)	11.8740(6)	10.0485(8)	10.0608(3)	8.3134(7)
b [Å]	12.0255(4)	12.1842(6)	11.0771(6)	20.0873(7)	9.7943(10)
c [Å]	15.0270(5)	15.6584(8)	20.0787(15)	13.5462(5)	18.142(2)
α [°]	78.301(3)	75.568(4)	97.100(5)	90	90
β [°]	71.871(3)	69.980(5)	99.637(6)	111.202(4)	90
γ [°]	62.217(3)	61.083(5)	114.841(6)	90	90
V [Å^3]	1808.32(10)	1853.44(16)	1952.0(2)	2552.30(15)	1477.2(3)
Z	2	2	2	2	2
$D_{calcd.}$ [g/cm^3]	1.261	1.273	1.270	1.274	1.409
$F(000)$	724	748	788	1044	652
Crystal size [mm]	0.21 × 0.14 × 0.07	0.21 × 0.09 × 0.07	0.27 × 0.18 × 0.07	0.37 × 0.18 × 0.10	0.41 × 0.17 × 0.16
θ range [°]	2.99–25.00	3.35–25.00	3.05–25.00	2.97–25.00	3.40–25.00
Index ranges	$-14 \le h \le 14$	$-14 \le h \le 14$	$-11 \le h \le 11$	$-11 \le h \le 11$	$-7 \le h \le 9$
	$-13 \le k \le 14$	$-14 \le k \le 14$	$-13 \le k \le 13$	$-18 \le k \le 23$	$-11 \le k \le 10$
	$-17 \le l \le 17$	$-18 \le l \le 18$	$-23 \le l \le 23$	$-13 \le l \le 16$	$-21 \le l \le 19$
Reflections collected	14533	13876	15728	11693	5514
Independent reflections	6349	6520	6844	4357	1350
R_{int}	0.0275	0.0716	0.0567	0.0410	0.0399
Completeness to θ = 25.00° [%]	99.7	99.8	99.7	97.0	99.7
Relative transmission factors	0.9510, 0.8626	0.9520, 0.8652	0.9539, 0.8375	0.9485, 0.8266	0.8720, 0.7142
Parameters	343	359	379	271	100
GOF	1.044	0.853	1.047	1.211	1.298
Final R indices [$I > 2\sigma(I)$][a,b]	R_1 = 0.0450	R_1 = 0.0521	R_1 = 0.0718	R_1 = 0.0553	R_1 = 0.0565
	wR_2 = 0.0950	wR_2 = 0.0679	wR_2 = 0.1595	wR_2 = 0.0920	wR_2 = 0.1221
R indices (all data)[a,b]	R_1 = 0.0665	R_1 = 0.1393	R_1 = 0.1049	R_1 = 0.0791	R_1 = 0.0623
	wR_2 = 0.1012	wR_2 = 0.0826	wR_2 = 0.1741	wR_2 = 0.0975	wR_2 = 0.1240

[a] $R_1 = \sum||F_o| - |F_c||/\sum F_o$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)]/[w(F_o^2)^2]\}^{1/2}$.

product was further purified by sublimation at 100–120 °C or by recrystallization from a hexane solution at –20 °C in 65% yield (147 mg, 0.21 mmol). Single crystals, suitable for X-ray diffraction, were obtained from the recrystallization. $C_{28}H_{62}Mo_2O_6$ (687.7): calcd. C 48.98, H 9.10; found C 48.62, H 9.36. ^{1}H NMR (C_6D_6, 298 K): δ = 5.25 (br., 8 H), 1.17 (s, 18 H), 1.13 (s, 36 H) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 88.62 (s), 76.67 (s), 34.27 (s), 32.22 (s), 26.36 (s) ppm. ^{95}Mo NMR (C_6D_6, 298 K): δ = 2593 ppm.

$Mo_2(OMBE)_2(Oneopent)_4$ (5): The complex was synthesized analogously to compound **4**. $Mo_2(OMBE)_6$ (200 mg, 0.29 mmol) was used and afforded **5** as yellow crystals in 89% yield (183 mg, 0.26 mmol), which were suitable for single-crystal X-ray diffraction. $C_{30}H_{62}Mo_2O_6$ (710.7): calcd. C 50.70, H 8.79; found C 50.33: H 8.69. ^{1}H NMR (C_6D_6, 298 K): δ = 5.70 (q, $^3J_{H,H}$ = 17.35 Hz, $^3J_{H,H}$ = 10.75 Hz, 2 H), 5.32 (br., 8 H), 4.92 (dd, $^3J_{H,H}$ = 17.35 Hz, $^2J_{H,H}$ = 1.34 Hz, 2 H), 4.66 (dd, $^3J_{H,H}$ = 10.75 Hz, $^2J_{H,H}$ = 1.34 Hz, 2 H), 1.62 (s, 36 H), 1.07 (s, 36 H) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 146.8 (s), 110.1 (s), 80.5 (s), 34.7 (s), 28.0 (s) ppm. ^{95}Mo NMR (C_6D_6, 298 K): δ = 2611 ppm.

$Mo_2(OMMP)_2(Oneopent)_4$ (6): The complex was synthesized analogously to compound **4** or with $Mo_2(Oneopent)_6$ as the starting material. $Mo_2(Oneopent)_6$ (264 mg, 0.37 mmol) and MMPOH (77 mg, 0.74 mmol) were used and afforded **6** as yellow crystals in a 76% yield (210 mg, 0.28 mmol), which were suitable for single-crystal X-ray diffraction. $C_{30}H_{66}Mo_2O_8$ (746.7): calcd. C 48.25, H 8.91; found C 48.39, H 8.24. ^{1}H NMR (C_6D_6, 298 K): δ = 5.38 (q, 8 H), 2.68 (s, 4 H), 2.55 (s, 6 H), 1.33 (s, 12 H), 1.20 (s, 36 H) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 87.9 (s, C-6), 80.5 (s, C-2), 77.9 (s, C-3), 57.4 (s), 34.3 (s), 27.6 (s), 26.5 (s) ppm. ^{95}Mo NMR (C_6D_6, 298 K): δ = 2602 ppm.

$Mo_2(OTerp)_4(Oneopent)_2$ (7): The complex was synthesized analogously to compound **4**, except that the complex could not be purified by sublimation. $Mo_2(OTerp)_6$ (200 mg, 0.18 mmol) was used and afforded **7** as yellow crystals in a 85% yield (159 mg, 0.16 mmol), which were suitable for single-crystal X-ray diffraction. $C_{50}H_{90}Mo_2O_6$ (979.1): calcd. C 61.33, H 9.26; found C 60.73, H 8.71. ^{1}H NMR (C_6D_6, 298 K): δ = 5.52 (br. s, 4 H), 5.31 (br., 4 H), 1.61 (br. s, 24 H), 1.26–2.14 (br. m, 7 H), 1.19 (br. s, 12 H), 1.17 (br. s, 12 H) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 133.2 (s), 121.2 (s), 89.0 (s), 83.5 (s), 46.4 (s), 34.4 (s), 31.3 (s), 29.2 (s), 27.5 (s), 26.3 (s), 24.4 (s), 23.2 (s) ppm. ^{95}Mo NMR (C_6D_6, 298 K): δ = 2481 ppm.

$Mo_2(O_2DMH)_2(OtBu)_2$ (8): A solution of $DMH(OH)_2$ (93 mg, 0.64 mmol) in hexane (2 mL) was added dropwise at room temperature to a solution of $Mo_2(OtBu)_6$ (200 mg, 0.32 mmol) in hexane (5 mL). After the solution had been stirred for 3 h, a yellow solid was obtained, which was filtered and washed with a small quantity of hexane. The product was further purified by recrystallization from dichloromethane at –20 °C in 89% yield (179 mg, 0.29 mmol). The single crystals obtained from the recrystallization were suitable for X-ray diffraction. $C_{24}H_{50}Mo_2O_6$ (626.5): calcd. C 46.01, H 8.04; found C 45.82, H 8.08. ^{1}H NMR ([D$_1$]chloroform, 298 K): δ = 1.77 (s, 8 H), 1.27 (s, 18 H), 1.11 (s, 24 H) ppm. ^{13}C NMR ([D$_1$]chloroform, 298 K): δ = 82.4 (s), 68.2 (s), 37.6 (s), 32.4 (s), 31.3 (s), 27.6 (s) ppm. ^{95}Mo NMR (C_6D_6, 298 K): δ = 2689 ppm.

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