An Update on W^{II} and Mo^{II} Carbonyl Precursors and Their Application in the Synthesis of Potentially Bio-Inspired Thiophenolate-Oxazoline Complexes

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Abstract. The synthesis of two new low-valent dicarbonyl complexes of tungsten $[W(CO)_2(SPh-oz)_2]$ (**3b**) and molybdenum $[Mo(CO)_2(SPh-oz)_2]$ (**4b**) coordinated by a bidentate thiolate-oxazoline ligand SPh-oz is reported. The thereby created coordination via two anionic sulfur atoms can be seen as biologically inspired as it reflects the first coordination sphere of the pterin cofactor found in molybdenum and tungsten enzymes. The in-situ preparation of the lithium salt Li(SPh-oz) (**1**) was described previously in literature, but analytical data was not available. A similar situation was found for the published syntheses of the low-valent metal precursors $[W(CO)_3(PPh_3)_2Cl_2]$ (**2a**), $[W_2(CO)_7Br_4]$ (**3a**) and $[Mo(CO)_4Br_2]$ where experimental procedures were unreliable and experimental data was inadequate or missing.

Introduction

Molybdenum and tungsten dependent enzymes are abundant and the molecular structure of many of them has been resolved. With the exception of nitrogenase, they all transfer oxygen to or from the substrate. Common to all known oxygen transferring enzymes is the coordination of the metal ion by one or two dithiolene moieties of the molybdopterin (MPT) cofactor. The central Mo/W atom has oxidation numbers ranging from +IV to +VI.^[1-3] Dithiolene ligands have been widely used as ligand environment analogues to mimic the immediate coordination sphere of the MPT cofactor.^[3,4] A variety of other ligands were investigated for the development of functional biomimetic models for OAT enzymes.^[2,5] Furthermore, the nitrogen rich environment found in the active sites of many other enzymes may in part be mimicked by functional groups such as imidazole or oxazoline. Therefore, we decided to develop molybdenum and tungsten complexes with a ligand that contains both an oxazoline heterocycle and a sulfur coordinating

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To the best of our knowledge this is the first report of a full characterization of the literature known compounds Li(SPh-oz) (1), $[W(CO)_3(PPh_3)_2Cl_2]$ (2a) and $[W_2(CO)_7Br_4]$ (3a). Furthermore the novel tetranuclear Mo-precursor $[Mo_4(CO)_7Br_{10}]$ (4a) was synthesized. The symmetric and asymmetric IR stretching frequencies of its seven carbonyl ligands were calculated using DFT and related to the experimental values. The molecular structures of the novel precursor compounds $[W(CO)_2(PPh_3)_2Cl_2]$ (2a'), $[PPh_3Cl]_2[WCl_6]$ (2b), $[Mo_4(CO)_7Br_{10}]$ (4a), the two complexes with the SPh-oz ligand $[W(CO)_2(SPh-oz)_2]$ (3b), $[Mo(CO)_2(SPh-oz)_2]$ (4b) and a new modification of $[W_2(CO)_7Br_4]$ (3a) were determined by single-crystal X-ray diffraction analysis.

site as potentially bio-inspired models. We found such a ligand in the literature known lithium thiophenolate oxazoline Li(SPh-oz) (1).

Few examples of transition metal complexes containing the ligand SPh-oz have been reported previously, none of them with molybdenum or tungsten. The cadmium and zinc complexes $[Cd(SPh-oz)_2]$ and $[Zn(SPh-oz)_2]$ have been obtained from a metathesis reaction of anhydrous MCl₂ with two equivalents of **1**.^[6] [Hg(SPh-oz)_2] has been realized by oxidative addition of the disulfide S₂(Ph-oz)₂ to elemental mercury.^[6] Furthermore, the preparation of the iron complexes $[Fe(SPh-oz)_2]$ and $[(SPh-oz)Fe-(\mu S)_2-Fe(SPh-oz)]$ has been described recently.^[7] However, we were surprised to find that in all of these publications no analytical data for the ligand Li(SPh-oz) (**1**) was reported.

The introduction of a thiophenolate ligand into a high-oxidation state metal complex is often hindered by the easy oxidation of the thio ligand to a disulfide under concomitant reduction of the metal. Hence, we searched for low oxidation state tungsten and molybdenum precursors which can potentially be oxidized in a subsequent step. Two possible precursors of the general type [M^{II}(CO)_nX₂] (M = Mo, W; *n* = 2, 3, 4, X = Cl, Br, I) have been described in literature. The phosphinestabilized, 18-electron species [M(CO)₃(PPh₃)₂X₂] (M = Mo, W; X = Cl, Br, I)^[8–13] and the less stable 16-electron species [M(CO)₄X₂] (M = Mo, W; X = Cl, Br, I).^[10,12–17] In particular, the W^{II} dichloride precursor [W(CO)₃(PPh₃)₂Cl₂]

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 $(2a)^{[8-10]}$ and the W^{II} dibromide $[W(CO)_4Br_2]^{[14,16,18]}$ were identified as suitable starting materials. Such precursors lead to tungsten carbonyl complexes which are generally stable and relatively easy to handle. Furthermore such M^{II} carbonyl complexes can be oxidized under relative mild conditions to yield the biological relevant M^{IV} species. Tertiary amine oxides, like pyridine *N*-oxide and trimethyl *N*-oxide, have been shown to transfer their oxygen atom quickly and relatively cleanly to metal centres.^[19,20] Other compounds that have been shown to transfer oxygen include $[Mo_2O_3(S_2P(OEt)_2)_4]$, Me₂SO, Ph₃PO, Ph₃AsO, Ph₂SeO, PhNN(O)Ph and more recently *meta*-chloroperoxybenzoic acid.^[19,21]

Results and Discussion

Ligand Synthesis

The thiophenolate oxazoline ligand Li(SPh-oz) (1) was prepared according to a modified literature procedure.^[6,7,22] Isolated 1 has been used for metathesis reactions previously, but a full analytical characterization was unavailable so far. The preparation of 1 occurs in two steps, as shown in Scheme 1. Commercially available Ph-oz is first *ortho*-lithiated and then sulfur is inserted into the Li–C bond.



Scheme 1. Synthesis of 1; a) *n*BuLi, pentane, -20 °C to room temp.; b) S₈, diethyl ether, 16 h.

The mechanism of *ortho*-lithiation of Ph-oz (step a) has been previously studied in great detail, however a detailed experimental protocol, including yields, was not published.^[23] Therefore we determined the isolated yields after step a. We found that the initial *ortho*-lithiation of Ph-oz is critical and does not proceed quantitatively with *n*BuLi, but instead crude yields of 70 to 80% were obtained. An increase in the base strength of the organolithium reagent resulted in a significant decrease of crude Li(Ph-oz). Roughly 44% crude product was obtained with *sec*-BuLi and the use of *tert*-BuLi yielded approximately 31% crude Li(Ph-oz) (cp. Table 1). This is attributed to a higher tendency of side reactions under the applied conditions, due to the increased reactivity of the organolithium reagent.

Table 1. Comparison of organolithium reagents ^{a)}.

Organolithium reagent	Molarity	in	Yield b)
nBuLi	1.6	hexanes	80 %
sec-BuLi	1.4	cyclohexane	44 %
tert-BuLi	1.7	pentane	31 %

a) Conditions: 1 mL Ph-oz in 20 mL pentane, addition of 1.05 equiv. LiR at -20 °C, stirring at room temp. for 1 hr., filtration, washing with cold pentane (2 × 10 mL) b) crude yield Li(Ph-oz).

Step b, the insertion of sulfur into the Li-C bond in diethyl ether has been described to take one to three hours.^[6,24] or overnight.^[7] We found that stirring overnight has the advantage of Li(SPh-oz) (1) precipitating from the reaction mixture and thereby simplifying work-up. 1 could be obtained in 49% isolated yield after centrifugation and removal of the supernatant liquid. The obtained microcrystalline pale yellow powder 1 exhibited good purity as assessed by ¹H and ¹³C NMR spectroscopy. In the ¹H NMR spectrum the four aromatic protons are baseline separated, resonating between 7.7-6.6 ppm. The ortho substitution is reflected in the coupling pattern of ddddd-ddd-dd which is clearly visible. The CH₂- and CH₃- group resonances show, as expected, sharp singlets in a ratio of 1:3. In contrast the in-situ product obtained from a one batch reaction in diethyl ether was impure, containing, amongst other compounds unreacted Ph-oz and S₂(Ph-oz)₂. In the direct inlet EI mass spectrum not only the [M⁺] signal of the lithiated species 1 (m/z = 213.2), but also the signals for the dimeric, trimeric and tetrameric modifications (m/z) = 426.4, 639.6,852.8) could be detected, pointing towards cluster formation. 1 is sparingly soluble in chlorinated solvents and moderately soluble in acetonitrile. Solutions of 1 in acetonitrile are of a blue-green to dark green color, even though being pale yellow as a solid. 1 can be stored for prolonged times under inert conditions, and only decomposes slowly under ambient conditions.

Precursor Synthesis

Even though several routes to WII-dihalide precursors are published, we found their experimental realization posing a number of difficulties. During the synthesis of $[W(CO)_3(PPh_3)_2Cl_2]$ (2a) according to the literature procedure^[9] it was observed that over-oxidation to W^{IV} or W^{VI} with concomitant carbonyl loss poses a serious problem, as the correct stoichiometry of Cl₂ is difficult to control when using condensed Cl₂ at -78 °C. Thus by following the literature protocol^[9], an orange, microcrystalline, carbonyl-free, diamagnetic compound was obtained in large quantities, which could be identified as [PPh₃Cl]₂[WCl₆] (**2b**) by single-crystal X-ray diffraction analysis (see SI). Presumably, excess of Cl₂ is responsible for the almost quantitative formation of 2b, instead of 2a (Scheme 2). Therefore the rigorous removal of even trace amounts of chlorine seems vital. Yet, even after vacuum drying the intermediate $[W(CO)_4Cl_2]$ for several hours Cl_2/HCl fumes leaving the Schlenk flask could be observed when purged with argon. Alternatively, the stoichiometric, dropwise addition of liquefied Cl_2 to a solution of $[W(CO)_6]$ has been described.^[8] However this method was rejected due to the extensive experimental setup.

The targeted precursor **2a** could finally be synthesized under modified conditions, albeit in poor yield. Compared to *McDonald* and co-workers^[9] the volume of Cl_2 was reduced to half, the reaction time was shortened, residual Cl_2 was evaporated extremely carefully and residual [W(CO)₆] was removed by sublimation giving a yellow microcrystalline material. IR spectra were recorded before and after sublimation,



Scheme 2. Synthesis of 2a and 2b; a) 2 equiv.PPh3, -78 °C b) excess Cl2, 2 equiv. PPh3, -78 °C.

both are in good agreement with literature, showing three CO stretches [IR (cm⁻¹): 2011 (s), 1930 (s), 1889 (s)].^[8,9,25] From this material single crystals suitable for X-ray diffraction analysis could be obtained from a saturated CH₂Cl₂ solution at -35 °C. Over the course of three months, the solution progressively turned red and dark red needles crystallized. Determination of the molecular structure revealed the 16-electron species [W(CO)₂(PPh₃)₂Cl₂] (2a', Figure 1) with only two carbonyl ligands coordinated to tungsten compared to the three in 2a. The lower coordination number in 2a' is equal to the one found in the analogous bromine compound [W(CO)₂(PPh₃)₂Br₂].^[26] However, the X-ray structure of the latter shows an octahedral geometry in contrast to that of 2a', in which the tungsten atom is found in an unusual trigonal prismatic surrounding. All bond lengths in 2a' are similar to those in the analogue bromine compound $[W(CO)_2(PPh_3)_2Br_2]$ (Table 2). It is interesting to note that a compound with the formula $[W(CO)_2(PPh_3)_2Cl_2]$ has been described previously. On the basis of IR data and its diamagnetic behavior it was suggested to be the dimer [W(CO)₂(PPh₃)₂Cl₂]₂, which was obtained by heating 2a in CH₂Cl₂ under reflux for four days and was described as light blue solid.^[8] The crystals of 2a' on the other hand were dark red.



Figure 1. ORTEP plot of **2a'** showing the atomic numbering scheme. The probability ellipsoids are drawn at 50% probability level.

The IR spectrum of crystalline of **2a'** displays two CO-stretches [IR (cm⁻¹): 1864 (s), 1843 (s)], in contrast to the three found for **2a** and the lowered frequencies demonstrate an increased double-bond character of the two remaining carbonyls. In the bromine analogous compound [W(CO)₃(PPh₃)₂Br₂] the removal of a carbonyl has been pre-

Table 2. Selected bond lengths /Å and angles /° for 2a'a).

W1C1	1.962(2)	C1-W1-Cl1	146.23(7)	Cl1–W1–Cl1 i	80.11(3)
W1-Cl1	2.4140(6)	Cl1-W1-P1 i	138.01(2)	C1-W1-P1	77.82(7)
W1-P1	2.4816(7)	P1-W1-P1 i	132.36(3)	Cl1-W1-P1	82.82(2)
C1-01	1.159(3)	C1-W1-C1 i	104.36(14)	C1-W1-P1 i	73.48(7)
		C1–W1–Cl1 i	96.17(7)	O1C1W1	176.3(2)

a) Symmetry transformations used to generate equivalent atoms: ⁱ⁾ 1-x, y, 3/2-z.

viously reported by refluxing in 1,2-dichloroethane or dichloromethane until a color change is observed.^[26,27] However, this reactivity has as yet not been mentioned at lowered temperatures.

 $[W(CO)_3(PPh_3)_2Cl_2]$ (**2a**) is a relatively air-stable precursor with a long shelf life, but its synthesis proved to be time-consuming and inefficient. Moreover, in subsequent reactions the coordinated PPh₃ has to be removed leading to additional steps in the work-up protocol. Therefore our focus was moved towards the phosphine and chlorine-free species $[W(CO)_4Br_2]$, which is obtainable by a straightforward oxidation reaction of $[W(CO)_6]$ with Br₂ in CH₂Cl₂.^[14,16] Compared to **2a**, by using bromine the stoichiometry of the reagents can be controlled much easier and therefore the risk of over-oxidation can be minimized (cp. Scheme 3). However, in our hands, the synthesis according to literature methods^[14,16] did not give the expected monomeric product, but yielded the dimeric species $[W_2(CO)_7Br_4]$ (**3a**).^[18]

The identity of 3a could be confirmed by NMR, IR spectroscopy and X-ray crystallography of single crystals grown from a saturated CH₂Cl₂ solution at -35 °C. In contrast to the published orthorhombic modification Pnma^[18], 3a crystallized in the new monoclinic modification $P2_1/n$ (see SI). The ¹³C NMR spectrum of 3a revealed two broad, weak signals in the ranges of 208.5-205.8 and 194.9-192.9 ppm (CD₂Cl₂, 75 MHz) equaling roughly one set of four carbons and one of three carbons. By raising the reaction temperature from $-78 \,^{\circ}C^{[14,16]}$ or $-60 \,^{\circ}C^{[18]}$ respectively, to $-20 \,^{\circ}C$ the yield could be improved significantly (see Exp. Sect.). 3a is moderately soluble in dichloromethane and can be dissolved in coordinating solvents like THF or acetonitrile with concomitant formation of W(CO)₃(Br)₂-solvent adducts. 3a can be synthesized efficiently and can be stored under inert atmospheres for prolonged times without decomposition. Therefore, 3a was used subsequently as the starting material of choice.

A similar procedure was employed for the preparation of a convenient molybdenum precursor. The oxidation of



Scheme 3. Synthesis of 3a; a) CH₂Cl₂, -78 °C, b) in-situ, -78 °C.



Scheme 4. Synthesis of 4a; a) CH₂Cl₂, -20 °C, b) in-situ, -20 °C.

 $[Mo(CO)_6]$ with one equivalent of Br₂ at -78 °C yielding orange $[Mo(CO)_4Br_2]$ has been published previously.^[14,16,17] It is described to be soluble in dichloromethane and to exhibit, depending on the medium, three or four carbonyl stretches.^[14] The published methods suggest a monomeric form with two equatorial bromine atoms in *cis*-configuration, albeit no X-ray structure is available. We, however, carried out the synthesis under conditions as optimized for $[W_2(CO)_7Br_4]$ (**3a**). The reaction at -20 °C yielded a brown to purple microcrystalline solid, which readily precipitated from CH₂Cl₂. In analogy to the W compound **3a** we expected the formation of a dimeric form with three bridging bromine atoms.

The identity of the reaction product could be elucidated by X-ray crystallography of single crystals grown from a saturated CH₂Cl₂ solution at -35 °C (Scheme 4). The structure refinement revealed the compound to be a linear, tetrameric molybdenum compound of the general formula $[Mo_4(CO)_7Br_{10}]$ (4a) (see Figure 2). Selected bond lengths and angles can be found in Table 3. 4a is the first example of a neutral nonakis(μ_2 halo)-tetra-metal molecule. The arrangement shows approximately Cs symmetry. The central Mo-Mo distance of Mo3–Mo4 2.7842(3) Å is much shorter than the two other Mo-Mo distances [Mo1-Mo3 3.4772(3) Å, Mo2-Mo4 3.4579(3) Å]. These in turn are distinctly shorter than the W1-W2 distance in **3a** [3.6799(6) Å] (see SI). The inner part of the molecule is composed of face-sharing MoBr₆ octahedra. The two terminal molybdenum atoms have coordination numbers of seven (see SI). The pattern found resembles the molecular structure of [MoBr₃] which crystallizes in chains of distorted octahedra.^[28,29] In [MoBr₃] bridging also occurs via three bromine atoms and every second Mo-Mo distance is significantly shorter (2.92 vs. 3.14 Å). This and the rather low magnetic susceptibility ($\mu_{exptl.} = 1.2 \text{ BM}$, $\mu_{theor.} = 3.87 \text{ BM}$) of [MoBr₃] hint at the presence of a Mo-Mo bond at the shorter bridges.^[29]

The resolved X-ray structure points to an oxidation number of +II for Mo1 and Mo2 (chain end) and of +III for the inner molybdenum atoms. Due to the short Mo3–Mo4 distance a Mo–Mo bond was assigned and thus **4a** was expected



Figure 2. ORTEP plot of **4a** showing the atomic numbering scheme. The probability ellipsoids are drawn at 50% probability level.

Table 3. Selected bond lengths /Å and angles /° for 4a.

Mo3–Mo4	2.7842(3)	Mo3–Br6	2.5643(4)	C2O2	1.130(4)
Mo1–C5	1.991(3)	Mo3-Br4	2.5882(3)	C5–O5	1.141(3)
Mo1–Br1	2.6372(4)	Mo4–Br5	2.5434(4)		
Mo1–Br4	2.7030(4)	Mo4–Br7	2.5465(3)	Mo3-Br4-Mo1	82.140(11)
Mo2–C4	2.031(3)	Mo4–Br6	2.5522(4)	Mo4–Br7–Mo3	66.043(10)
Mo2–Br8	2.6607(3)	Mo4–Br9	2.6011(4)	Mo4–Br9–Mo2	81.299(11)

to exhibit diamagnetic behavior. Despite being a tetramer $[Mo_4(CO)_7Br_{10}]$ (4a) displays similar stability and reactivity to 3a. The formation of the tetramer, instead of the dimer is attributed to a higher reactivity of $[Mo(CO)_6]$ compared to $[W(CO)_6]$. Studies are currently underway to develop milder reaction conditions that favor the formation of the Mo^{II} dimer.

IR spectroscopy of compound **4a** revealed three major CO frequencies with several smaller shoulders as shown in Figure 3. For a better understanding, theoretical calculations using DFT methods were performed. The experimentally found CO frequencies of **4a** were compared to those calculated for the published monomeric structure $[Mo(CO)_4Br_2]$,^[14,16,17] the targeted dimeric $[Mo_2(CO)_7Br_4]$ and the obtained tetrameric $[Mo_4(CO)_7Br_{10}]$ (**4a**) form. Figure 3 shows the CO region of the measured spectrum and the calculated, scaled IR frequencies of the monomeric, dimeric and tetrameric form. Table 4 presents the analysis of the given IR signals. The monomeric form displaying a distorted octahedral geometry shows four IR signals matching two of the three measured IR





Figure 3. Carbonyl region of the measured and calculated, scaled IR spectra, of the possible monomeric $[Mo(CO)_4Br_2]$, dimeric $[Mo_2(CO)_7Br_4]$ and tetrameric $[Mo_4(CO)_7Br_{10}]$ (4a) products.

Table 4. Analysis of the IR signals presented in Figure 3.

	Wave number /cm ⁻¹	IR Intensity /km·mol ⁻¹	Vibrational mode ^[a]
Monomer	2020	530.4	AS stretch of equatorial CO
	2028	851.0	AS stretch of axial CO
	2043	1438	AS stretch all four CO
	2109	126.7	S stretch all four CO
Dimer	1977	1004	AS stretch of C6 & C7
	1987	390.3	AS stretch of C5 & C6/C7
	2023	812.2	AS stretch of C2 & C3
	2033	958.6	AS stretch of C1/C3 & C4
	2038	182.3	AS stretch of C1/C3 & C2/C4
	2049	1179	S stretch of C5, C6, C7
	2100	720.3	S stretch of C1, C2, C3, C4
Tetramer	1979	1000	AS stretch of C6 & C7
	1986	454.0	AS stretch of C5 & C6/C7
	2031	760.6	AS stretch of C2 & C3
	2034	923.9	AS stretch of C1/C3 & C4
	2042	183.2	AS stretch of C1/C3 & C2/C4
	2050	1451	S stretch of C5, C6, C7
	2103	1182	S stretch of C1, C2, C3, C4

a) Bold carbonyls: main contribution to respective vibration; AS: asymmetrical, S: symmetrical, /: same motion in vibration.

bands. The calculated spectra of the dimeric and tetrameric form are almost identical. The IR modes of the dimeric and tetrameric geometry fit to all three experimental bands. Hence the computational results support the asymmetric structure of **4a** similar to the corresponding tungsten complex **3a**. Furthermore, the M–CO bond lengths were calculated and found to be in good agreement with those of the X-ray crystal structure (max. rel. deviation: 1.5%; cp. SI).

The microcrystalline material of **4a** which readily precipitated from the reaction mixture was analyzed by ¹³C NMR spectroscopy. We were not able to detect ¹³C NMR resonances after measuring 53 hours on a 500 MHz spectrometer, which is in contrast to the tungsten species **3a**. The elemental analysis of the bulk material indicates it to be mainly the tetrametic compound $[Mo_4(CO)_7Br_{10}]$ (**4a**), although the determined values are slightly too low indicating the presence of some impurities which we were as yet unable to remove. However, the low carbon value (found: C 5.28%; calcd.: C 6.10%) excludes the material to be the dimeric compound $[Mo_2(CO)_7Br_4]$ (calcd.: C 11.88%).

Coordination Compounds

The novel complexes $[W(CO)_2(SPh-oz)_2]$ (**3b**) and $[Mo(CO)_2(SPh-oz)_2]$ (**4b**) could be synthesized from the respective M^{II} bromine precursor **3a/4a** and Li(SPh-oz) (**1**) in a straightforward metathesis reaction (see Scheme 5). A solution of the ligand in acetonitrile was slowly added to the dissolved precursor at room temp. The respective precursors were dissolved in acetonitrile in order to break up the μ -bromo bridges prior to the reaction, as evidenced by CO evolution. Extraction with toluene, followed by recrystallization from a concentrated toluene solution yielded orange (**3b**) or purple (**4b**) crystals. Satisfying yields (47 %) could be achieved for **3b**, whereas **4b**

could only be obtained in 23% yield. The novel compounds were characterized by NMR and IR spectroscopy, elemental analysis and X-ray crystallography. Interestingly, the ¹³C NMR spectra reveal rather deshielded carbonyl carbons, resonating at $\delta = 244.7$ and 246.5 ppm, respectively. The IR resonance frequencies of 1917, 1807 and 1935, 1831 cm⁻¹ indicate reduced triple bond character of the carbonyl ligands. The tungsten species exhibits slightly lower triple bond character and slightly less deshielded carbonyl carbons hinting that tungsten is capable of stronger π -back bonding than molybdenum (cp. Table 5). On the other hand the C=N stretching frequencies of 3b and 4b are virtually identical, resonating at 1593 and 1592 cm⁻¹ respectively. This indicates a reduction of the double bond character compared to the free ligand where the C=N resonance can be found at 1627 cm⁻¹. Both compounds are soluble in polar organic solvents, solutions are relatively air stable, but slowly decompose after several days. Microcrystalline powders of 3b and 4b can be exposed to air for several weeks without decomposition.



Scheme 5. Synthesis of 3b and 4b; a) acetonitrile, room temp.

 Table 5. Comparison of the carbonyl ligands in 3b and 4b.

	¹³ C NMR /ppm ^{a)}	IR /cm ⁻¹	M1–C1 /Å	C1–O1 /Å	M1-C1-O1 /° ^{b)}
3b	244.7	1917, 1807	1.9718(15)	1.1589(19)	4.24
4b	246.5	1935, 1831	1.9811(11)	1.1538(14)	4.91

a) CD₂Cl₂; b) Deviation from ideal linear geometry.

Single crystals of **3b** and **4b** suitable for structural analysis by X-ray crystallography were obtained from a saturated toluene solution at -25 °C. Molecular views of **3b** and **4b** are shown in Figure 4 and selected bond lengths are given in Table 6. Both compounds exhibit very similar structural properties. The metal atoms are coordinated in a distorted octahedral arrangement by two, symmetry-equivalent SPh-oz ligands. The two CO ligands are *cis* orientated towards one another, as expected due to the strong trans-effect of carbonyls. The weaker coordinating nitrogen lone pair takes up the positions trans to the CO ligands. A Cambridge Structure Database search revealed that there are only two other published six-coordinate, dicarbonyl compounds with two sulfur and two nitrogen atoms coordinated to tungsten. However neither has a bidentate S,N-donor ligand like 3b. One structure shows octahedral coordination as well, and the other exhibits an unusual trigonal prismatic coordination.^[30,31] In the case of molybdenum. 4b is the first example of a dicarbonyl complex coordinated by two bidentate S and/or N donor ligands. There are three other six-coordinate dicarbonyl compounds displaying a similar first coordination sphere, but using mono- and bidentate ligands.^[32,33] The deviation from ideal octahedral geometry is reflected, amongst other, by the angle of the two cis oriented carbonyl ligands, which is $C1^{i}$ W1–C1 = 77.46(8)° and C1-Mo1-C1ⁱ⁾ = 77.97(6) respectively. In **3b** and **4b** all M-C, M-S and M-N distances lie within the expected range of other published structures.^[30-33] However, the Mo-C, Mo-S and Mo-N bonds are somewhat longer than the corresponding W-X bonds.

Conclusions

Within this paper we report on the synthesis of two new tungsten and molybdenum complexes **3b** and **4b** coordinated by a thiolate-oxazoline ligand. This ligand creates an anionic sulfur coordination sphere around the metal atom, which renders **3a** and **4b** starting points for bio-inspired model complexes of enzymes like W-dependent *Acetylene Hydratase* or Mo-dependent *Oxotransferases*. In further studies the oxidation of the M^{II} atoms to the biologically relevant M^{IV} state under CO loss will be addressed. We re-investigated the published syntheses for ligand **1** and the metal precursors **2a** and **3a** and added full analytical details where this information was missing so far. The synthesis of the novel tetranuclear molybd-



Figure 4. ORTEP plot of 3b and 4b showing the atomic numbering scheme. The probability ellipsoids are drawn at 50% probability level.



Table 6. Selected bond lengths /Å and angles /° for 3b and 4b^{a)}.

	M = W	M = Mo		M = W	M = Mo		M = W	M = Mo
M1-C1	1.9718(15)	1.9811(11)	C1-M1-N13 i	172.47(5)	172.37(4)	C1-M1-S1 i	92.48(4)	92.18(3)
M1-N13	2.2190(12)	2.233 - 3(9)	S1-M1-S1 i	170.645(17)	171.795(14)	C1-M1-S1	94.82(4)	94.20(3)
M1-S1	2.3636(4)	2.3669(3)	C1-M1-C1 i	77.46(8)	77.97(6)	N13-M1-S1	82.69(3)	82.95(2)
C101	1.1589(19)	1.1538(14)	C1-M1-N13	97.12(5)	96.46(4)	N13-M1-S1 i	90.61(3)	91.21(2)
			N13-M1-N13 i	88.73(6)	89.54(4)	O1C1M1	175.76(13)	175.09(10)

a) Symmetry transformations used to generate equivalent atoms: ⁱ⁾ 1-x, y, 3/2-z.

enum precursor 4a could be achieved. Further studies are underway towards monomeric or dimeric modifications of 4a in order to increase the atom efficiency of subsequent reactions.

Experimental Section

General Procedures. If not stated otherwise, all manipulations were performed under an atmosphere of Ar employing standard Schlenk and glovebox techniques. Chlorine 2.8 was dried with P4O10 and H2SO4. Ph-oz (4,4-dimethyl-2-phenyl-2-oxazoline) was degassed prior to use and sulfur was recrystallized from boiling toluene. All other chemicals were purchased from commercial sources and were used without further purification. Solvents were purified via a Pure Solv Solvent Purification System. All NMR spectra were measured on a Bruker Avance III 300 MHz spectrometer. ¹H and ¹³C NMR spectroscopy chemical shifts are given in ppm and are referenced to residual protons in the solvent. Spectra were obtained at 25 °C. Solid state IR spectra were measured with a Bruker ALPHA-P Diamant ATR-FTIR spectrometer at a resolution of 2 cm⁻¹. Solution IR spectra were measured using a Bruker ALPHA-T probe head at a resolution of 2 cm⁻¹. Signal intensities are assigned according to their relative intensities as strong (s), medium (m). Weak or very weak resonances are omitted. All IR-bands are listed in cm⁻¹. Mass spectra were recorded with an Agilent Technologies 5975C inert XL MSD instrument using the direct insertion technique.

Elemental analyses were carried out at the Graz University of Technology using a Heraeus Vario Elementar automatic analyzer (2a/b, 3b, 4a/b) and at the Microanalytical Laboratory at the University of Vienna using a EuroVector EA3000 (4a). The Br contents of 3a and 4a were measured at the Microanalytical Laboratory at the University of Vienna by digestion and subsequent titration against a 0.1 N AgNO_3 solution. The tungsten and molybdenum content of 3a and 4a was determined with an Agilent 7500ce ICP-MS instrument in helium collision mode using external calibration. Further details are described in the supporting information.

Computational Details: Input geometries were obtained using Avogadro.^[34] DFT-calculations were performed in the gas phase using the B3-LYP functional as implemented in TURBOMOLE.^[35] Structures were pre-optimized using the standard double- ζ quality basis set def2-SVP.^[36,37] Vibrational analysis was performed on structures optimized with a triple- ζ quality basis set def2-TZVP.^[37,38] Effective core potentials (ecp-28-mwb) and corresponding basis sets were applied to the molybdenum central atom(s). Infrared signals were scaled by 0.9654 for comparison to experimental data.^[39] Plots were obtained using QtiPlot.^[40]

Crystallographic Details: X–ray data collection was performed with a Bruker AXS SMART APEX 2 CCD diffractometer by using graphitemonochromated Mo- K_{α} radiation (0.71073 Å) from a fine-focus sealed tube at 100 K. SHELXS-97^[41] was used as structure solution and structure refinement program. Full-matrix least-squares on F^2 was employed as refinement method. Further details on the solution of the structures can be found in the SI. Crystallographic data (excluding structure factors) for the structures of the compounds reported herein have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers. The following identification numbers have been assigned: CCDC-916659 (**2a**⁴), CCDC -916658 (**2b**), CCDC -916660 (**3a**), CCDC -916661 (**3b**), CCDC -918776 (**4a**) and CCDC -916662 (**4b**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U. K. [Fax: (international)b44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Li(SPh-oz) $(1)^{[7]}$, $[W(CO)_3(PPh_3)_2Cl_2]$ $(2a)^{[9]}$ and $[W_2(CO)_7Br_4]$ $(3a)^{[14,16,18]}$ were prepared by modifications of the respective literature procedures.

Synthesis of Li(SPh-oz) (1): 4,4-dimethyl-2-phenyl-2-oxazoline (Phoz, 1 mL, 98 mmol) was dissolved in pentane (20 mL), the solution was cooled to -20 °C (NaCl/ ice) and nBuLi (1.6 M in hexanes, 3.7 mL, 1.0 mmol) was added dropwise. After stirring the reaction mixture for 1 h at room temp. the supernatant liquid was removed. The white precipitate was washed with cold pentane (2 \times 10 mL) to yield crude Li(Ph-oz) (0.809 g, 4.5 mmol, 80%). Li(Ph-oz) was suspended in diethyl ether and S₈ (0.143 g, 4.5 mmol) was added. Stirring overnight, centrifugation and removal of the supernatant liquid yielded 1 as pale yellow, microcrystalline solid. Yield (overall): 0.583 g (2.7 mmol, 49 %) ¹**H NMR** (300 MHz, CD₃CN): δ = 7.64 (dd, J = 8.0, 1.7 Hz, 1 H, Ar), 7.48 (dd, J = 8.1, 1.0 Hz, 1 H, Ar), 6.88 (ddd, J = 8.1, 7.0, 1.7 Hz, 1 H, Ar), 6.69 (ddd, J = 8.3, 7.0, 1.4 Hz, 1 H, Ar), 3.99 (s, 2) H, CH₂), 1.36 (s, 6 H, 2 CH₃). ¹³C NMR (75 MHz, CD₃CN): δ = 165.80, 160.31, 138.83, 131.34, 129.25, 126.98, 118.94, 77.86, 68.71, 28.41. IR: 2966 (m), 1627 (s), 1463 (m), 1355 (m), 1316 (m), 1249 (m), 1206 (m), 1133 (m), 1088 (m), 1039 (s), 969 (m), 768 (m), 728 (s),690 (s),648 (m), 512 (m), 432 (m). EI-MS: m/z 213.2 [M⁺], 426.4 [M⁺]₂, 639.6 [M⁺]₃, 852.8 [M⁺]₄.

Synthesis of $[W(CO)_3(PPh_3)_2Cl_2]$ (2a): $[W(CO)_6]$ (2.512 g, 7.1 mmol) was added to a Schlenk flask containing condensed chlorine (10 mL, acetone/ dry ice). The yellow slurry was stirred for 20 min at -78 °C. Keeping the reaction vessel at -78 °C, the chlorine was evaporated in vacuo into a trap cooled to -196 °C. PPh₃ (3.755 g, 14.3 mmol), dissolved in 50 mL CH₂Cl₂, was added dropwise over 90 min to the bright yellow residue. After stirring at -78 °C for 15 min, the reaction mixture was allowed to warm to room temperature, whereupon a bright yellow solid precipitated. Removal of the solvent in vacuo yielded crude 2a as yellow microcrystalline solid. Residual [W(CO)₆] was removed by sublimation under vacuum at 40 °C. Yield: 1.504 g (1.7 mmol, 24%) ¹**H** NMR (300 MHz, CD₂Cl₂): δ = 7.68– 7.27 (m, 30 H). ¹³C NMR (75 MHz, CD_2Cl_2): $\delta = C_q$ obscured, 136.06–125.89. ³¹**P** NMR (121 MHz, CD_2Cl_2): $\delta = 14.81$, 9.13. IR (CO): 2011, 1930, 1889. . C₃₉H₃₀Cl₂O₃P₂W (863.35): calcd. C 54.26, H 3.50%; found: C 52.85, H 3.22%.

Single crystals of **2a'** suitable for structure determination by X-ray crystallography were obtained from a supersaturated CH_2Cl_2 solution at -35 °C. **IR** 1864 (s), 1843 (s).

Synthesis of [PPh₃Cl]₂[WCl₆] (2b): Chlorine (approx. 120 mL) was condensed (acetone/ dry ice) into a Schlenk flask containing [W(CO)₆] (15.438 g, 43.9 mmol). The resulting dark red solution was stirred for 1 h at -78 °C. Keeping the reaction vessel at -78 °C, the chlorine was evaporated in vacuo into a trap cooled to -196 °C. PPh₃ (23.312 g, 88.9 mmol) dissolved in CH₂Cl₂ (80 mL) was added dropwise over an hour to the dark red residue. After stirring at -78 °C for 30 min, the reaction mixture was allowed to warm to room temperature. Gas evolution was observed and an orange solid started to precipitate, which was isolated by filtration and washed with diethyl ether $(3 \times 50 \text{ mL})$ to yield **2b** as a bright orange microcrystalline solid. Yield: 38.360 g (39 mmol, 88%). Single crystals of 2b suitable for structure determination by X-ray crystallography were obtained by slow evaporation of CH₂Cl₂ at room temp. ¹H NMR (300 MHz, CD_2Cl_2): $\delta = 7.98-7.74$ (m, 30 H). ¹³C NMR (75 MHz, CD_2Cl_2): $\delta =$ 148.65, 139.25 (d, J = 3.1 Hz), 137.71 (d, J = 13.2 Hz), 136.39, 134.64 (d, J = 14.8 Hz), 131.79, 119.23 (d, J = 93.4 Hz). ³¹**P** NMR (121 MHz, CD_2Cl_2 : $\delta = 72.55$. **IR** 1436 (s), 1107 (s), 995 (m), 756 (s), 727 (s), 684 (s), 575 (s), 510 (s), 449 (m) . $C_{36}H_{30}Cl_8P_2W$ (992.03): calcd. C 43.59, H 3.05%; found: C 43.50, H 2.72%

Synthesis of [W₂(CO)₇Br₄] (3a): At –20 °C (NaCl/ ice) Br₂ (0.5 mL, 9.8 mmol) was added dropwise to a suspension of [W(CO)₆] (3.130 g, 8.9 mmol) in CH₂Cl₂ (approx. 50 mL). The solution was stirred at –20 °C for 2 h after which the resulting dark brown slurry was allowed to warm to room temp. Removal of the solvent in vacuo yielded crude **3a**. Residual [W(CO)₆] was removed by sublimation under vacuum at 40 °C. Yield: 3.496 g, (4.0 mmol, 89%). Single crystals of **3a** suitable for structure determination by X-ray crystallography were obtained from a saturated solution in CH₂Cl₂ at –35 °C. ¹³C NMR (75 MHz, CD₂Cl₂): δ = 208.5–205.8, 194.9–192.9. **IR** (CO): 2107, 2022, 2008, 1974, 1966, 1949, 1936. . C₇Br₄O₇W₂· 0.1 WBr₆ (949.97): calcd. C 8.85, Br 38.70, W 40.65%; found: C 8.67, Br 39.07, W 40.67%.

Synthesis of [W(CO)₂(SPh-oz)₂] (3b): Li(SPh-oz) (1) (0.204 g, 0.94 mmol) and [W₂(CO)₇Br₄] (3a) (0.202 g, 0.23 mmol) were dissolved in acetonitrile in separate flasks and the ligand solution was slowly added to the precursor. Stirring for 90 min and evaporation to dryness yielded crude 3b, which was further purified by extraction with toluene and crystallization, as its 1:1 toluene adduct, from a supersaturated toluene solution at -25 °C. Yield: 0.160 g (0.21 mmol, 47 %) Single crystals suitable for structure determination by X-ray crystallography were obtained from toluene at -35 °C. ¹H NMR (300 MHz, CD_2Cl_2): $\delta = 7.89$ (d, J = 7.7 Hz, 2 H, Ar), 7.84 (d, J = 8.0 Hz, 2 H, Ar), 7.56–7.48 (m, 2 H, Ar), 7.35 (t, J = 7.3 Hz, 2 H, Ar), 3.91 (d, J = 8.2 Hz, 2 H, CH₂), 2.80 (d, J = 8.3 Hz, 2 H, CH₂), 0.83 (s, 6 H, CH₃), 0.52 (s, 6 H, CH₃). ¹³C NMR (75 MHz, CD₂Cl₂): δ = 244.66, 167.29, 165.42, 132.01, 130.94, 130.47, 125.67, 77.65, 74.17, 28.78, 23.04. IR (neat): $\tilde{v} = 1917$, 1807 cm⁻¹ (CO), 1593 (C=N). EI-MS: m/z652.1 [M⁺]. . C₃₁H₃₄N₂O₄S₂W (746.58): calcd. C 49.87, H 4.59, N 3.75%; found: C 49.60, H 4.01, N3.96%.

Synthesis of $[Mo_4(CO)_7Br_{10}]$ (4a): At -25 °C (ice/ MgCl₂) Br₂ (0.65 mL, 12.7 mmol) was added dropwise to a suspension of $[Mo(CO)_6]$ (3.010 g, 11.4 mmol) in CH₂Cl₂ (50 mL). The reaction mixture was stirred at -25 °C for 1 h. Afterwards the dark purple slurry was allowed to warm to room temp. Removal of the solvent by filtration yielded crude 4a. Residual $[Mo(CO)_6]$ was removed by sublimation under vacuum at 40 °C. Yield: 3.362 g (2.4 mmol, 96%) Single crystals of 4a suitable for structure determination by X-ray crystallography were obtained from a saturated solution in CH_2Cl_2 at -35 °C. ¹³C NMR: No signal could be detected after 53 h on a 500 MHz NMR spectrometer. **IR** (CO): 2119, 2054, 1987. C₇Br₁₀O₇Mo₄ (1378.95): calcd. C 6.10, Br 57.95, Mo 27.84%; found: C 5.28. Br 55.61, Mo 25.61%.

Synthesis of [Mo(CO)₂(SPh-oz)₂] (4b): Li(SPh-oz) (1) (0.200 g, 0.94 mmol) and [Mo₄(CO)₇Br₁₀] (4a) (0.168 g, 0.12 mmol) were separately dissolved in acetonitrile and the ligand was slowly added to the precursor. Stirring for 90 min followed by evaporation to dryness yielded crude 4b, which was further purified by extraction with toluene and crystallization as its 1:1 toluene adduct at -25 °C. Yield: 0.032 g (0.06 mmol, 23%) Single crystals of 4b suitable for structure determination by X-ray crystallography were obtained from a toluene solution at -25 °C. ¹**H NMR** (300 MHz, CD₂Cl₂): $\delta = 7.92$ (ddd, J = 11.0, 7.9, 1.4 Hz, 4 H, Ar), 7.49 (td, J = 7.6, 1.6 Hz, 2 H, Ar), 7.34 (td, J = 7.6, 1.3 Hz, 2 H, Ar), 3.85 (d, J = 8.2 Hz, 2 H, CH₂), 2.95 (d, J = 8.2 Hz, 2 H, CH₂), 0.64 (s, 6 H, CH₃), 0.42 (s, 6 H, CH₃).b ¹³C NMR $(75 \text{ MHz}, \text{ CD}_2\text{Cl}_2)$: $\delta = 246.48, 166.26, 160.19, 131.50, 130.93,$ 130.11, 125.44, 77.93, 72.21, 27.94, 22.69. **IR** (neat): $\tilde{v} = 1935$, 1831 cm⁻¹ (CO) 1592 (C=N). . C₃₁H₃₃MoN₂O₄S₂ (659.09): calcd. C 56.61, H 5.06, N 4.26%; found C 55.72, H 4.13, N 5.31.

Supporting Information (see footnote on the first page of this article): Description of the structures, selected bond lengths and angles and molecular views of compounds $[PPh_3Cl)[WCl_6]$ (2b) and $[W_2(CO)_7Br_4]$ (3a). Packing view of $[Mo_4(CO)_7Br_{10}]$ (4a). Details on elemental analyses of 3a and 4a. Calculated bond lengths of compounds $[Mo(CO)_4Br_2]$, $[Mo_2(CO)_7Br_4]$ and 4a.

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