

N-Heterocyclic carbenes as ligands in high-valent molybdenum and tungsten complexes ¹

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Abstract

Oxometal complexes of molybdenum and tungsten in high oxidation states form stable adducts with 1,3-dimethylimidazoline-2-ylidene (L) **1**. The first 'carbene' complexes of molybdenum(VI) [MoO₂Cl(L)₃]Cl (**3a**) and tungsten(VI) WO₂Cl₂(L)₂ (**4b**) are reported.

Keywords: Molybdenum(VI); Tungsten(VI); Imidazoline-2-ylidene; Heterocyclic carbenes

1. Introduction

N-Heterocyclic carbenes derived from imidazolium and pyrazolium salts by deprotonation are well-established ligands in organometallic chemistry, and they particularly cover the chemistry of low oxidation-state transition metal complexes [2,3]. The *N*-heterocyclic carbene L = 1,3-dimethylimidazoline-2-ylidene (**1**) seems to reveal universal ligand properties in metal coordination chemistry [1–4]. In addition to pronounced σ -donor properties (as for example seen in the complex [ClBeL₃]Cl [**5**]), this ligand is normally stable against oxidation when coordinated in oxometal complexes [6]. To extend the chemistry of oxomolybdenum and oxotungsten complexes, which are known as excellent epoxidation catalysts, we now report the synthesis of the first stable molybdenum(VI) and tungsten(VI) carbene derivatives.

2. Results and discussion

MoO₂Cl₂(thf)₂ (**2a**) and WO₂Cl₂(thf)₂ (**2b**) are formed as intermediates by dissolving MoO₂Cl₂,

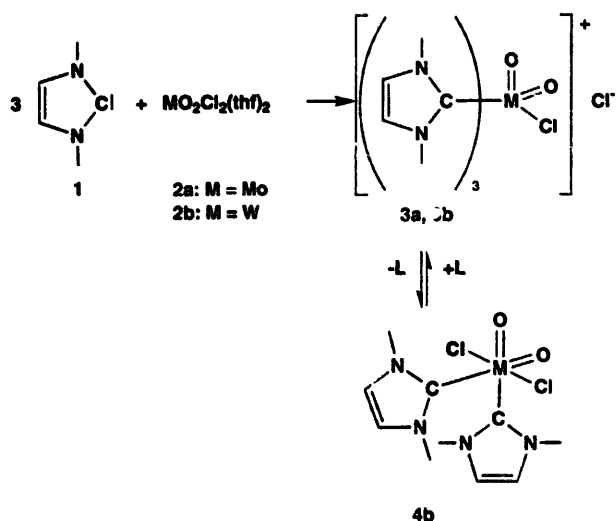
MoO₂Cl₂(dmf)₂ and WO₂Cl₂ in thf at –20 °C. The new carbene 'adducts' **3a** and **4b** are prepared by adding three equivalents of free carbene **1** (dissolved in thf) at –20 °C to thf solutions of **2a** and **2b** respectively.

After stirring for 2 h, purple (molybdenum) **3a** and green (tungsten) **4b** solids precipitate (Scheme 1). The proposed structures of **3a** and **4b** are shown in Fig. 1; they are in accord with the analytical data derived from NMR, IR, elemental analysis and mass spectroscopy. The ¹H and especially the ¹³C NMR spectra prove that the complexation of the ligand **1** is to the metal center of the molybdenum and the tungsten derivatives. The signal of the carbene–C nucleus is shifted ca. 40 ppm to higher field, upon complexation of the ligand to the metal: δ = 177 ppm (**3a**, **3b**) and at 187 ppm (**4b**) compared with δ = 215 ppm of the free ligand **1**. Two signal groups of the carbene ligand can be observed for **3a**. In contrast to **3a**, only one signal group of the carbene ligand is detected for **4b**.

Three different signal groups are also found for another molybdenum complex Mo(CO)₃L₃ (three carbene ligands not chemically equivalent). Interestingly, the ¹³C NMR carbene–C signals of **3a**, **3b**, and **4b** are shifted to lower field in comparison with known low-oxidation state complexes (190–210 ppm) [7]. This observation is in accord with the chemical shift of the rhenium(VII)–'carbene' complex CH₃ReO₃L₂, δ C(carbene) = 176.1 ppm (CDCl₃, 20 °C). Elemental analyses and the NMR data (Table 1) of the isolated complexes **3a**, **4b** prove that **3a**, represents a triscarbene

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¹ Heterocyclic carbenes, part 6. In memoriam Professor Takaya, who died in October 1995 during the Vth Königstein/Kreuth Conference on Organometallic Chemistry. Preceding communication within this series, see Ref. [1].



Scheme 1. Synthesis of the carbene adducts **3a**, **4b** (L = 1,3-dimethylimidazolin-2-ylidene).

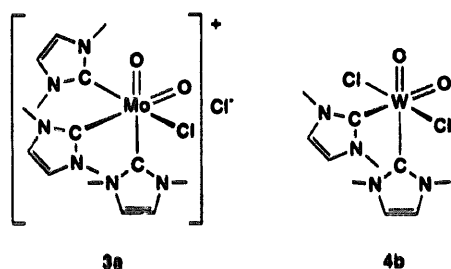


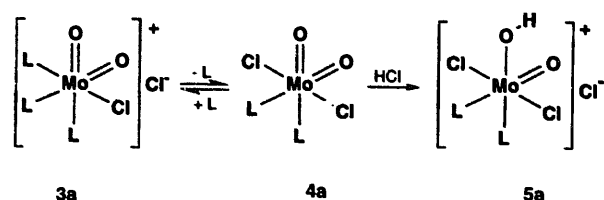
Fig. 1. Proposed structures of the 'carbene'-complexes **3a** and **4b**.

complex while **4b** exhibits only two of these ligands. (In the case of the tungsten complex **4b**, the elemental analysis indicates impurities of an oxotungsten species). In the IR spectra the stretching bands of the *cis*-dioxomolybdenum and the *cis*-dioxotungsten fragment are found, each with two absorptions of ca. 910 cm^{-1} (**3a**) and ca. 940 cm^{-1} (**4**). The characteristic absorptions of the carbene ligand are also present. Complex **3a** should exhibit the two equivalent carbene ligands in the plane of the *cis*-dioxo metal core. The third carbene ligand is then located trans to the chloro ligand.

Table 1
NMR data of the carbene complexes **3a** and **4b** at 20°C

Compound	$^1\text{H}(\delta, \text{ppm, CDCl}_3)^a$		$^{13}\text{C}(\delta, \text{ppm, CDCl}_3)$		
	N-CH ₃	C=CH-N	N-CH ₃	C=CH-N	Carbene-C
3a	4.23, 4.03	7.42, 6.96	36.5, 39.9	123.0, 123.2	177.2, 177.7
4b	4.23	6.99	40.2	123.5	187.7
Decompos.	3.58	6.85	35.3	121.9	134.7
Mo(CO) ₃ (L) ₃	3.48, 3.50,	6.93, 6.95,	—	—	—
	3.57	6.96			
CH ₃ ReO ₃ (L) ₂	3.52	6.90	37.1	122.7	176.1

^a All carbene **1** signals in ^1H NMR are singlets; L = heterocyclic carbene **1**.



Scheme 2. Protonation and decomposition of **3a** (l = 1,3-dimethylimidazolin-2-ylidene). Further hydrolysis of the intermediate **5a** leads to molybdate(VI).

The resulting cationic complex is quite rare a feature for molybdenum(VI) species [8]. In the electroneutral tungsten complex **4a**, the carbene ligands are also in the plane of the *cis*-dioxotungsten core.

Decomposition of **3a** can be followed by ^{13}C NMR spectroscopy. An additional different signal group is detected at $\delta = 177.0, 123.2$ and 36.4 ppm after 1 h in ordinary CDCl_3 and $\text{DMSO}-d_6$, proving the presence of the complex $\text{MoO}_2\text{Cl}_2\text{L}_2$ **3b**, which then decomposes by treatment with the acidic solvent CDCl_3 to the imidazolium salt, as seen in the NMR spectra (Table 1). The initial step of this degradation reaction is the protonation of the oxygen atom of **3a**, enhancing the Lewis acidity of the metal center which is then easily attacked by water (Scheme 2). After protonation, rapid hydrolysis takes place to yield molybdate(VI).

3. Conclusion

Our results show that the *N*-heterocyclic carbene **1** is so flexible in its electronic structure that it tolerates even strongly Lewis acidic metals in high oxidation states. However, hydrolysis is a prevalent feature here, so catalytic applications in the presence of water (e.g. olefin epoxidation with H_2O_2) are outside the scope of application [9]. A comparison with known dioxometal halides containing σ -donor molecules shows that cationic molybdenyl complexes of type $[\text{MoO}_2\text{ClL}_3]^+ \text{Cl}^-$ are not known for ligands other than the present heterocyclic carbene, while electroneutral derivatives

$\text{MoO}_2\text{Cl}_2\text{L}_2$ (L = dmf, OPPh_3 , OAsPh_3 , pyridine) are legion [10–12].

4. Experimental part

All experiments have been carried out by using standard Schlenk techniques and completely dry solvents (water content: less than 1 ppm; Karl–Fischer titrations). The starting material MoO_2Cl_2 , $\text{MoO}_2\text{Cl}_2(\text{dmf})_2$ and WO_2Cl_2 are prepared as described in the literature [13–15]. The quality of these extremely air- and moisture-sensitive starting materials, that contain normally hydrolytic by-products, governs the success of the described synthesis. They thus must be purified several times before use.

The NMR spectra were recorded on an FT-Jeol GX-400 instrument. NMR solvents were 'freeze-pump-thaw' degassed and stored over molecular sieves before use. Elemental analyses were performed in the Microanalytical Laboratory of our institute. δ -values (NMR) are given in ppm.

4.1. Purification of the precursor complexes MoO_2Cl_2 , $\text{MoO}_2\text{Cl}_2(\text{dmf})_2$, WO_2Cl_2

MoO_2Cl_2 can be purified by sublimation. MoO_2Cl_2 was triply sublimed in order to remove the decomposition products (as 'molybdenum blue'). The dimethylformamide adduct of the MoO_2Cl_2 was prepared as described in Ref. [14], but washed five times with dry acetone, thus obtaining a pure material in low yield but as an acid-free product. In the case of the tungsten precursor the only way to purify WO_2Cl_2 is subliming WOCl_4 because sublimation at the WO_2Cl_2 step is not possible.

4.2. Chlorotris(1,3-dimethylimidazoline-2-ylidene)dioxomolybdenum(VI) chloride (3a)

300 mg (1.5 mmol) of MoO_2Cl_2 are dissolved in 20 ml of cool thf (-20°C). Three equivalents of the free carbene 1 (thf solution, 4.5 mmol) were then added at -20°C . A purple precipitate forms within 2 h. After filtration the product was washed twice with diethyl ether and was then dried for 2 days in an oil-pump vacuum. Yield: 0.82 g (37%) of 3a. Anal. Found: C, 35.91; H, 5.05; Cl, 13.33; Mo, 20.11; N, 15.95. $\text{C}_{15}\text{H}_{24}\text{Cl}_2\text{MoN}_6\text{O}_2$ (3a). Calc.: C, 36.29; H, 4.83; Cl, 14.33%; Mo, 20.06; N, 16.93. ^1H NMR (CDCl_3 , 400 MHz, 20°C): δ = 7.42 (s, CH, 4H), 6.96 (s, CH, 2H), 4.23 (s, CH_3 , 12H), 4.03 (s, CH_3 , 6H). ^{13}C NMR (CDCl_3 , 100.1 MHz, 20°C): δ = 177.7 (NCN), 177.2 (NCN), 123.21 (NCHCHN), 122.96 (NCHCHN), 39.75 (CH_3), 36.53 (CH_3). IR (KBr, cm^{-1}): $\nu(\text{C}-$

$\text{H}, \text{CC}-\text{H})$ = 3200–3100(s), $\nu(\text{C}-\text{H}, \text{aliph.})$ = 2915(m), $\nu(\text{C}=\text{C}, \text{arom})$ = 1576(s), $\nu(\text{Mo}=\text{O})$ = 916(m), 912(m).

4.3. Dichlorobis(1,3-dimethylimidazoline-2-ylidene)dioxotungsten(VI) (4b)

200 mg (0.7 mmol) of tungstenylchloride (WO_2Cl_2) were dissolved in 20 ml of cooled thf (-20°C). Three equivalents of the free carbene 1 (thf solution, 2.2 mmol) were then added at -20°C . A green precipitate forms within 2 h. After filtration the product was washed twice with diethyl ether and then dried for 2 days in an oil-pump vacuum. Yield: 0.87 g (26%) of 4b. ^1H NMR (CDCl_3 , 400 MHz, 20°C): δ = 6.99 (s, CH, 4H), 4.23 (s, CH_3 , 12H). ^{13}C NMR (CDCl_3 , 100.1 MHz, 20°C): δ = 187.68 (NCN), 123.45 (NCHCHN), 40.23 (CH_3). IR (KBr, cm^{-1}): $\nu(\text{C}-\text{H}, \text{CC}-\text{H})$ = 3200–3100(s), $\nu(\text{C}-\text{H}, \text{aliph.})$ = 2898(m), $\nu(\text{C}=\text{C}, \text{arom})$ = 1554(s), $\nu(\text{W}=\text{O})$ = 945(m), 940(m).

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