

# Dioxomolybdenum(VI) complexes containing *N*-heterocyclic carbenes

Elena Mas-Marzá<sup>a</sup>, Patrícia M. Reis<sup>b</sup>, Eduardo Peris<sup>a,\*</sup>, Beatriz Royo<sup>b,\*</sup>

<sup>a</sup> *Departamento de Química Inorgánica y Orgánica, Universitat Jaume I, Avenida Vicente Sos Baynat s/n 12071 Castellón, Spain*

<sup>b</sup> *Instituto de Tecnologia Química e Biológica da Universidade Nova de Lisboa, Quinta do Marquês, EAN, Apt. 127, 2781-901 Oeiras, Portugal*

Received 14 December 2005; received in revised form 6 February 2006; accepted 6 February 2006

Available online 20 March 2006

## Abstract

Compound  $\text{MoO}_2\text{Cl}_2(\text{THF})_2$  reacts with two equivalents of 1,3-dialkyl substituted 4,5-dimethylimidazol-2-ylidenes to give the dioxomolybdenum(VI) complexes  $\text{MoO}_2\text{Cl}_2(\text{L}^{\text{R}})_2$  [ $\text{R} = \text{Me}$  (**1**), *i*-Pr (**2**)]. Treatment of  $\text{MoO}_2\text{Cl}_2(\text{THF})_2$  with one equivalent of the *N*-heterocyclic carbenes  $\text{L}^{\text{Me}}$ ,  $\text{L}^{\text{i-Pr}}$  and  ${}^{\text{C}1}\text{L}^{\text{n-Bu}}$  ( $\text{L}^{\text{Me}} = 1,3,4,5\text{-tetramethylimidazol-2-ylidene}$ ,  $\text{L}^{\text{i-Pr}} = 1,3\text{-diisopropyl-4,5-dimethylimidazol-2-ylidene}$ , and  ${}^{\text{C}1}\text{L}^{\text{n-Bu}} = 1,3\text{-dibutyl-4,5-dichloroimidazol-2-ylidene}$ ) affords the monocarbene adducts  $\text{MoO}_2\text{Cl}_2(\text{L}^{\text{R}})$  [ $\text{R} = \text{Me}$  (**3**), *i*-Pr (**4**)] and  $\text{MoO}_2\text{Cl}_2({}^{\text{C}1}\text{L}^{\text{n-Bu}})$  (**5**), respectively. Decomposition of complexes **1–5** affords a molybdenum oxychloride anion  $[\text{Mo}_2\text{O}_5\text{Cl}_4]^{2-}$  as an imidazolium salt.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** *N*-heterocyclic carbenes; Molybdenum; Oxo

## 1. Introduction

Since the successful isolation of *N*-heterocyclic carbenes (NHCs) by Arduengo and co-workers [1], NHCs derived from imidazolium salts have been established as universal ligands in the preparation of a large variety of organometallic species with many metals, affording new routes to enhanced catalytic species [2]. Although most of the NHC–metal complexes reported to date refer to late transition metals in low oxidation states, a few examples concerning the coordination of these ligands to high oxidation state species have been reported [3–5]. Regarding the studies of *N*-heterocyclic carbene complexes of molybdenum, these are scarce, and most of them concern carbonyl molybdenum (0) complexes [6]. The only example of a NHC–Mo(VI) complex was described by Herrmann and co-workers ten years ago [7]. The reaction of three equivalents of 1,3-dimethylimidazol-2-ylidene with  $\text{MoO}_2\text{Cl}_2(\text{THF})_2$  afforded the tris-NHC cationic complex

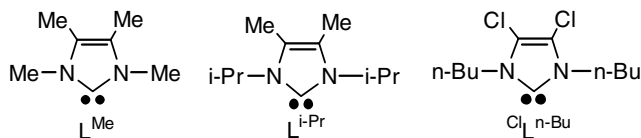
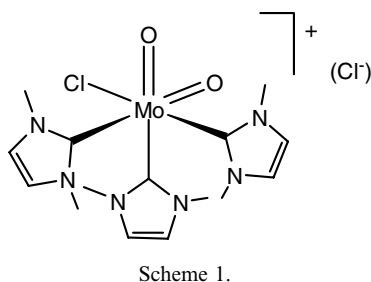
$[\text{MoO}_2\text{Cl}(\text{L})_3]\text{Cl}$  shown in Scheme 1 ( $\text{L} = 1,3\text{-dimethylimidazol-2-ylidene}$ ) [7]. In the same work, the formation of a bis-NHC of the type  $\text{MoO}_2\text{Cl}_2(\text{NHC})_2$  was proposed as a possible intermediate in the decomposition pathway of the cationic triscarbene complex, although it was not detected [7]. With all this in mind, we decided to study the coordination of the *N*-heterocyclic-carbenes  $\text{L}^{\text{Me}}$ ,  $\text{L}^{\text{i-Pr}}$  and  ${}^{\text{C}1}\text{L}^{\text{n-Bu}}$  ( $\text{L}^{\text{Me}} = 1,3,4,5\text{-tetramethylimidazol-2-ylidene}$ ,  $\text{L}^{\text{i-Pr}} = 1,3\text{-diisopropyl-4,5-dimethylimidazol-2-ylidene}$ , and  ${}^{\text{C}1}\text{L}^{\text{n-Bu}} = 1,3\text{-dibutyl-4,5-dichloroimidazol-2-ylidene}$ , see Chart 1) to  $\text{MoO}_2\text{Cl}_2(\text{THF})_2$ , with the initial aim to study what is the influence of the modification of the steric and electronic properties of the NHC ligands in the stability and reactivity of the complexes obtained. Herein we describe a synthetic route leading to the preparation of lower NHC-containing Mo(VI) complexes, namely  $\text{MoO}_2\text{Cl}_2(\text{NHC})_2$  and  $\text{MoO}_2\text{Cl}_2(\text{NHC})$ , whose reactivity is described.

## 2. Experimental

All manipulations were carried out under nitrogen standard Schlenk techniques. Solvents were purified by stan-

\* Corresponding authors.

E-mail addresses: [eperis@qio.uji.es](mailto:eperis@qio.uji.es) (E. Peris), [broyo@itqb.unl.pt](mailto:broyo@itqb.unl.pt) (B. Royo).



standard procedures and distilled under nitrogen prior to use. NMR spectra were recorded with a Bruker AMX 300 spectrometer. Infrared spectra were recorded with a Unicam Mattson Model 7000 FTIR spectrophotometer using KBr pellets. Elemental analyses were performed in our laboratories (ITQB). Standard literature methods were utilized for the preparation of  $[\text{MoO}_2\text{Cl}_2]$  [8], the 1,3-dialkyl-4,5-dimethylimidazol-2-ylidenes were readily available by the reduction of the corresponding imidazol-2(3H)-thiones with potassium in boiling THF [9], while the 1,3-dibutyl-4,5-dichloroimidazol-2-ylidene was obtained by deprotonation of the corresponding imidazolium salts by  $n\text{-BuOK}$  [10].

### 2.1. Dichlorobis(1,3,4,5-tetramethylimidazol-2-ylidene)-dioxomolybdenum(VI) $\text{MoO}_2\text{Cl}_2(\text{L}^{\text{Me}})_2$ (**1**)

A solution of 1,3,4,5-tetramethylimidazol-2-ylidene (0.74 g, 6.00 mmol) in THF (20  $\text{cm}^3$ ) cooled to  $-20^\circ\text{C}$ , was added to a suspension of  $\text{MoO}_2\text{Cl}_2$  (0.60 g, 3.00 mmol) in THF (30  $\text{cm}^3$ ) at  $-20^\circ\text{C}$  and the reaction mixture was stirred for 1 h at low temperature. The product,  $\text{MoO}_2\text{Cl}_2(\text{L}^{\text{Me}})_2$  (**1**), immediately precipitated as a purple powder directly from the reaction mixture, and was isolated by filtration and washed twice with cold THF to yield pure solid of **1** (1.14 g, 85%). Anal. Calc. for  $\text{C}_{14}\text{H}_{24}\text{Cl}_2\text{N}_4\text{O}_2\text{Mo}$  (447.22): C, 37.60; H, 5.41; N, 12.53. Found: C, 37.52; H, 5.70; N, 12.10%. Selected IR data (KBr):  $\nu(\text{MoO})$  942, 916 vs  $\text{cm}^{-1}$ .

### 2.2. Dichlorobis(1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene)dioxomolybdenum(VI) $\text{MoO}_2\text{Cl}_2(\text{L}^{\text{i-Pr}})_2$ (**2**)

A solution of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (0.54 g, 3.01 mmol) in THF (10  $\text{cm}^3$ ) cooled to  $-20^\circ\text{C}$ , was added to a suspension of  $\text{MoO}_2\text{Cl}_2$  (0.30 g, 1.50 mmol) in THF (20  $\text{cm}^3$ ) at  $-20^\circ\text{C}$  and the reaction mixture was stirred for 2 h at low temperature. The product,  $\text{MoO}_2\text{Cl}_2(\text{L}^{\text{i-Pr}})_2$  (**2**), immediately precipitated as a yellow powder and was isolated by filtration and washed twice

with cold THF to yield pure solid of **2** (0.63 g, 75%). Anal. Calc. for  $\text{C}_{22}\text{H}_{40}\text{Cl}_2\text{N}_4\text{O}_2\text{Mo}$  (559.43): C, 47.23; H, 7.21; N, 10.01. Found: C, 47.51; H, 7.29; N, 10.30%. Selected IR data (KBr):  $\nu(\text{MoO})$  920, 880 vs  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  6.38 (m, 2H,  $\text{NCH}(\text{CH}_3)_2$ ), 2.27 (s, 6H,  $\text{C}=\text{CCH}_3$ ), 1.48 (d,  $J_{\text{H,H}} = 6$  Hz, 12H,  $\text{NCH}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  179.8 ( $\text{MoC}_{\text{carbene}}$ ), 129.7 ( $\text{C}=\text{CCH}_3$ ), 56.4 ( $\text{NCH}(\text{CH}_3)_2$ ), 24.2 ( $\text{NCH}(\text{CH}_3)_2$ ), 13.6 ( $\text{C}=\text{CCH}_3$ ).

### 2.3. Dichloro(1,3,4,5-tetramethylimidazol-2-ylidene)dioxomolybdenum(VI) $\text{MoO}_2\text{Cl}_2(\text{L}^{\text{Me}})$ (**3**)

A solution of 1,3,4,5-tetramethylimidazol-2-ylidene (0.82 g, 6.60 mmol) in THF (20  $\text{cm}^3$ ) cooled to  $-20^\circ\text{C}$ , was added to a suspension of  $\text{MoO}_2\text{Cl}_2$  (1.31 g, 6.60 mmol) in THF (30  $\text{cm}^3$ ) at  $-20^\circ\text{C}$ . When the addition was completed a green yellowish solution was rapidly formed. The reaction mixture was stirred for 1 h at low temperature and a small amount of a purple solid containing **1** was filtered off. The filtrate was concentrated in vacuo to dryness to afford a green yellowish solid of the title compound **3** (1.73 g, 81%), which was washed with *n*-hexane. Anal. Calc. for  $\text{C}_7\text{H}_{12}\text{Cl}_2\text{N}_2\text{O}_2\text{Mo}$  (323.03): C, 26.03; H, 3.74; N, 8.67. Found: C, 26.24; H, 3.87; N, 8.85%. Selected IR data (KBr):  $\nu(\text{MoO})$  955, 914 vs  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  3.90 (s, 6H,  $\text{NCH}_3$ ), 2.14 (s, 6H,  $\text{C}=\text{CCH}_3$ ).

### 2.4. Dichloro(1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene)dioxomolybdenum(VI) $\text{MoO}_2\text{Cl}_2(\text{L}^{\text{i-Pr}})$ (**4**)

A solution of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (0.86 g, 4.77 mmol) in THF (20  $\text{cm}^3$ ) cooled to  $-20^\circ\text{C}$ , was added to a suspension of  $\text{MoO}_2\text{Cl}_2$  (0.95 g, 4.77 mmol) in THF (30  $\text{cm}^3$ ) at  $-20^\circ\text{C}$ . When the addition was completed an orange solution was rapidly formed. The reaction mixture was stirred for 1 h at low temperature and a small amount of a yellow solid containing **2** was filtered off. The filtrate was concentrated in vacuo to dryness to afford an orange solid of the title compound **4** (1.43 g, 80%), which was washed with *n*-hexane. Anal. Calc. for  $\text{C}_{11}\text{H}_{20}\text{Cl}_2\text{N}_2\text{O}_2\text{Mo}$  (379.14): C, 34.85; H, 5.32; N, 7.39. Found: C, 34.98; H, 5.27; N, 7.07%. Selected IR data (KBr):  $\nu(\text{MoO})$  954, 913 vs  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  5.06 (m, 2H,  $\text{NCH}(\text{CH}_3)_2$ ), 1.41 (s, 6H,  $\text{C}=\text{CCH}_3$ ), 0.96 (d,  $J_{\text{H,H}} = 6.6$  Hz, 12H,  $\text{NCH}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  175.2 ( $\text{MoC}_{\text{carbene}}$ ), 126.4 ( $\text{C}=\text{CCH}_3$ ), 54.8 ( $\text{NCH}(\text{CH}_3)_2$ ), 21.5 ( $\text{NCH}(\text{CH}_3)_2$ ), 10.7 ( $\text{C}=\text{CCH}_3$ ).

### 2.5. Dichloro(1,3-dibutyl-4,5-dichloroimidazol-2-ylidene)-dioxomolybdenum(VI) $\text{MoO}_2\text{Cl}_2(\text{L}^{\text{n-Bu}})$ (**5**)

A solution of 4,5-dichloro-1,3-dibutylimidazol-2-ylidene (0.20 g, 0.80 mmol), previously dissolved in THF (20  $\text{cm}^3$ ) cooled to  $-20^\circ\text{C}$ , was added to a suspension of  $\text{MoO}_2\text{Cl}_2$  (0.16 g, 0.80 mmol) in THF (10  $\text{cm}^3$ ) at  $-20^\circ\text{C}$ . When the

addition was completed an orange solution was rapidly formed. The reaction mixture was stirred for 2 h at low temperature and was filtered. The filtrate was concentrated in vacuo to dryness to afford an orange solid of the title compound **5** (0.28 g, 80%), which was washed with *n*-hexane. Anal. Calc. for  $C_{11}H_{18}Cl_4N_2O_2Mo$  (448.03): C, 29.49, H, 4.05, N, 6.25. Found: C, 29.34; H, 4.45; N, 5.79%. Selected IR data (KBr)  $\nu(\text{MoO})$ : 949, 913 vs  $\text{cm}^{-1}$ .

2.6. 1,3-Diisopropyl-4,5-dimethylimidazolium pentaoytetracloridedimolybdate(VI),  $[\text{Mo}_2(\mu\text{-O})(\mu\text{-Cl})_2\text{Cl}_2\text{O}_4][\text{HL}^{i\text{-Pr}}]_2(6)$

A slow diffusion of diethyl ether ( $10 \text{ cm}^3$ ) in a solution of **4** (0.04 g, 0.11 mmol) in  $\text{CH}_2\text{Cl}_2$  ( $1 \text{ cm}^3$ ), under inert atmosphere and low temperature ( $-10^\circ\text{C}$ ), afforded in three days compound **6** (0.02 g, 40%), as colourless crystalline solid. Anal. Calc. for  $C_{22}H_{42}Cl_4N_4O_5Mo_2$  (776.28): C, 34.04, H, 5.45, N, 7.22. Found: C, 34.12; H, 5.39; N, 7.20%. Selected IR data (KBr)  $\nu(\text{MoO})$ : 942, 912 vs  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  8.41 (s, NCHN), 4.48 (m, 2H, NCH( $\text{CH}_3$ ) $_2$ ), 2.23 (s, 6H, C=CCH $_3$ ), 1.47 (d,  $J_{\text{H,H}} = 6.6 \text{ Hz}$ , 12H, NCH( $\text{CH}_3$ ) $_2$ ).

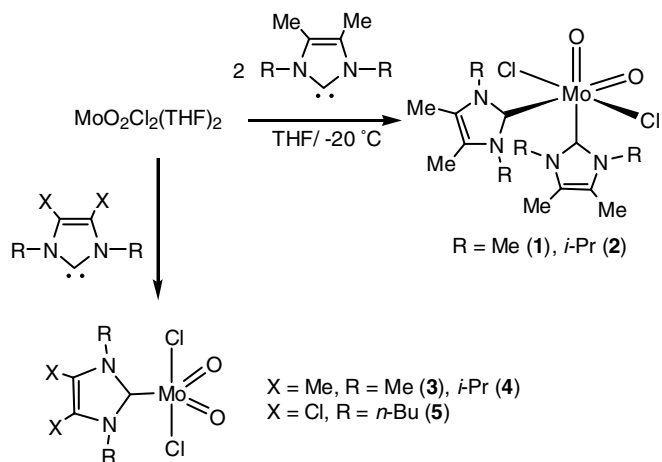
2.7. X-ray diffraction studies of compound **6**

A single crystal of compound **6** was mounted on a glass fiber in a random orientation. Data collection was performed at room temperature on a Siemens Smart CCD diffractometer using graphite monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The diffraction frames were integrated using the SAINT package.

Space group assignment was based on systematic absences, *E* statistics and successful refinement of the structures. The structure was solved by direct methods with the aid of successive differences Fourier maps and were refined using the SHELXTL 5.1 software package. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were assigned to ideal positions and refined using a riding model.

### 3. Results and discussion

Treatment of a suspension of  $\text{MoO}_2\text{Cl}_2(\text{THF})_2$  in THF with two equivalents of 1,3-dialkyl substituted 4,5-dimethylimidazol-2-ylidenes at  $-20^\circ\text{C}$  afforded the dioxomolybdenum(VI) complexes  $\text{MoO}_2\text{Cl}_2(\text{L}^{\text{R}})_2$  [ $\text{R} = \text{Me}$  (**1**), *i*-Pr (**2**)] as purple and yellow powders, respectively (Scheme 2). Compound  $\text{MoO}_2\text{Cl}_2(\text{L}^{\text{Me}})_2$ , **1**, is insoluble in most of common organic solvents, e.g., THF, diethyl ether, dichloromethane, toluene and *n*-hexane, but it dissolves in acetonitrile providing a purple solution that rapidly decomposes leading to the formation of a white solid.  $\text{MoO}_2\text{Cl}_2(\text{L}^{i\text{-Pr}})_2$ , **2**, is insoluble in THF, diethyl ether, and *n*-hexane and soluble in chloroform, dichloromethane and toluene. Both complexes **1** and **2** are extremely air and moisture sensitive. Thermal decomposition has also been



Scheme 2.

observed when the solids are kept under inert atmosphere at room temperature for several hours, although they can be stored during days at low temperature ( $-10^\circ\text{C}$ ). The infrared spectra show the characteristic asymmetric and symmetric Mo=O stretches at 916 (**1**), 880 (**2**) and 942 (**1**), 920 (**2**)  $\text{cm}^{-1}$ , respectively, in the region where other *cis*- $\text{MoO}_2\text{Cl}_2\text{L}_2$  complexes appear [11]. Lower IR frequencies were observed for the previously reported tris-NHC complex  $[\text{MoO}_2\text{Cl}(\text{1,3-dimethylimidazol-2-ylidene})_3]\text{Cl}$  (916, 912  $\text{cm}^{-1}$ ) [7], probably due to the presence of three highly electron-donating NHC-ligands. The differences in the M–O stretching frequencies between **1** and **2** may be attributed to the higher basicity of the *N*-isopropyl substituted imidazolylidene ligand, compared to *N*-methyl substituted one, in accordance with the recently published works by Yates [12] and Abram [13]. Both  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra could not be recorded for complex **1** due to its rapid decomposition in solution. The  $^1\text{H}$  NMR spectrum of **2** displays a multiplet at  $\delta$  6.38 for the CH proton of the isopropyl group, a singlet at  $\delta$  2.27 for the methyls bonded to the olefinic carbons of the carbene ligand and a doublet at  $\delta$  1.48 for the methyl protons of the isopropyl group. Its  $^1\text{H}$  NMR spectrum also shows an additional group of signals at  $\delta$  10.82, 4.49, 2.24 and 1.67 ppm, due to the imidazolium cation  $[\text{HL}^{i\text{-Pr}}]^+$  formed by decomposition of **2** in solution. If the NMR sample is recorded after being kept for 10 h at room temperature, its spectrum showed only the signals due to  $[\text{HL}^{i\text{-Pr}}]^+$ . The  $^{13}\text{C}$  NMR spectrum of **2** displayed an only signal for the carbene-carbon at 179.8 ppm, a value that is similar to that shown for the previously reported compound  $[\text{MoO}_2\text{Cl}(\text{1,3-dimethylimidazol-2-ylidene})_3]\text{Cl}$  (177 ppm) [7].

Reaction of  $\text{MoO}_2\text{Cl}_2(\text{THF})_2$  with one equivalent of 1,3-dialkyl substituted 4,5-dimethylimidazol-2-ylidenes in THF at  $-20^\circ\text{C}$  affords  $\text{MoO}_2\text{Cl}_2(\text{L}^{\text{R}})$  [ $\text{R} = \text{Me}$  (**3**), *i*-Pr (**4**)] (Scheme 2). Compounds **3** and **4** are isolated as green yellowish and orange solids, respectively, and were characterized by elemental analysis,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and infrared spectroscopy. Complex **3** is soluble in THF, chlo-

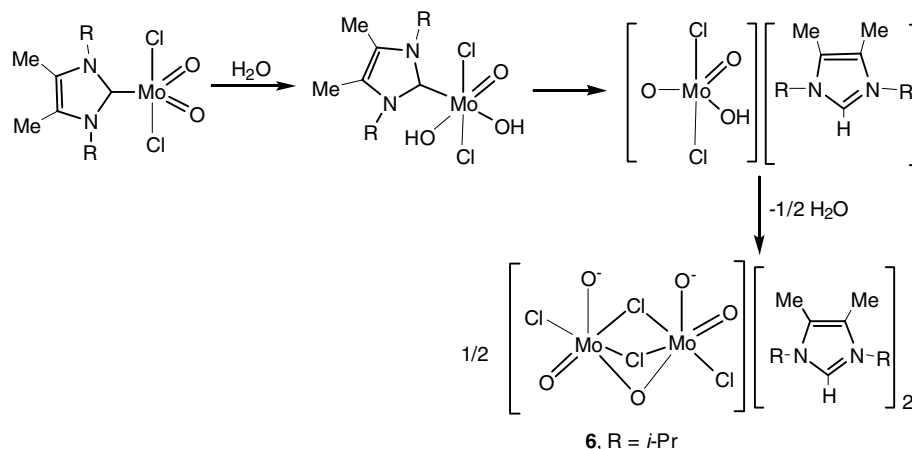
roform and dichloromethane and insoluble in toluene and *n*-hexane, whereas **4** dissolves readily in toluene and benzene. The pentacoordinated monocarbene complexes **3** and **4** are sensitive to moisture, traces of water lead to decomposition. The infrared spectra of **3**, **4** and **5** show the characteristic asymmetric and symmetric Mo=O stretches at values ranging from 949–955 and 913–914 cm<sup>-1</sup>. These frequencies are higher than those shown for related bis-(this paper) and tris-NHC complexes [7]. As mentioned above, the reduction of the number of the strong electron-donating NHC-ligands is consistent with an increase of the Mo=O stretching frequencies.

The introduction of chloro-substituents in the 4 and 5 positions of the azole ring is known to significantly reduces the electron-donating character of the imidazolylidene ligand, as has been shown from both experimental [14] and theoretical [12] points of view. The reaction of MoO<sub>2</sub>Cl<sub>2</sub>(THF)<sub>2</sub> with one equivalent of 1,3-dibutyl-4,5-dichloroimidazol-2-ylidene (C<sup>1</sup>L<sup>*n*-Bu</sup>) at -20 °C yielded MoO<sub>2</sub>Cl<sub>2</sub>(C<sup>1</sup>L<sup>*n*-Bu</sup>) (**5**) as an orange solid. Products with more than one 1,3-dibutyl-4,5-dichloroimidazol-2-ylidene could not be obtained when the reaction is carried out with two or three equivalents of the carbene C<sup>1</sup>L<sup>*n*-Bu</sup>. This is in agreement with the results recently published by Abram and co-workers, who observed that the number of NHCs introduced in a series of oxorhenium complexes depends on the electron-donating nature of the carbene, the more electron-donating the carbene, the higher the number of ligands [13]. In this sense, 4,5-dimethyl substituted NHCs always provide complexes with general formula [ReOCl(NHC)<sub>4</sub>]<sup>2+</sup> [4,15] (complexes with less than four carbenes could not be obtained), while non-substituted and triazolylidene NHCs provide ReOCl<sub>3</sub>(NHC)<sub>2</sub> [5] and [ReO(OMe)Cl<sub>2</sub>(NHC)(PPh<sub>3</sub>)], respectively.

The <sup>1</sup>H NMR spectra of **3** and **4** indicate the equivalence of the 1,3-dialkyl substituted-4,5-dimethyl-2-ylidene. For complex **3** it was not possible to record the <sup>13</sup>C NMR spectrum due to its rapid decomposition in solution; its <sup>1</sup>H NMR spectrum displays two resonances at δ 3.90 and

2.14 ppm for the methyls bonded to the N atoms and the olefinic carbons of the carbene ligand, respectively. The <sup>1</sup>H NMR spectrum also shows additional resonances at δ 3.84 and 2.20 ppm due to the imidazolium cation [HL<sup>Me</sup>]<sup>+</sup> formed by decomposition of **3** in solution. Long standing solutions of **3** in the NMR tube afford the NMR signals due to the decomposition products. For complex **4**, the <sup>1</sup>H NMR spectrum shows a singlet at δ 1.41 ppm for the methyls bonded to the olefinic carbons, a multiplet at δ 5.06 ppm and a doublet at δ 0.96 ppm for the isopropyls bonded to the nitrogen atom of the carbene ligand. The <sup>13</sup>C NMR spectrum of **4** displays the characteristic carbene-carbon resonance appeared at 175.2 ppm. It seems likely that the carbene ligand in **3–5** is disposed in the equatorial plane of a trigonal bipyramidal arrangement, as observed for other five-coordinate dioxo molybdenum(VI) complexes, such as [MoO<sub>2</sub>(OSiPh<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)] [16].

We tried to obtain single crystals of **1–5** by slow diffusion of diethyl ether in CH<sub>2</sub>Cl<sub>2</sub> concentrated solutions of the compounds, under inert atmosphere and low temperature (-10°C). In particular, a solution of **4** in CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O afforded colorless crystals suitable for X-Ray diffraction. The structure of the crystallized product consisted of the dimeric complex [Mo<sub>2</sub>(μ-O)(μ-Cl)<sub>2</sub>Cl<sub>2</sub>O<sub>4</sub>][HL<sup>*i*-Pr</sup>]<sub>2</sub>, **6** (the molecular structure is available in the supporting information) (Scheme 3). A similar complex with [NBu<sub>4</sub>]<sup>+</sup> as counter-cation has already been reported [17]. Obviously, the structure does not correspond to any of the expected species, but it gave us some clues about the decomposition mechanism of the Mo(VI)-NHC compounds. Herrmann proposed a decomposition mechanism for [MoO<sub>2</sub>Cl(NHC)<sub>3</sub>](Cl) involving, first the elimination of one of the NHC ligands to provide MoO<sub>2</sub>Cl<sub>2</sub>(NHC)<sub>2</sub> and then acid hydrolysis to yield the hydroxo-NHC complex [MoO(OH)Cl<sub>2</sub>(NHC)<sub>2</sub>](Cl) [7]. According to the decomposition product that we obtained, we believe that the process rather occurs by a hydrolytic mechanism such as that shown in Scheme 3. Traces of water should be added to the electron deficient complex **4** in the form of an OH



Scheme 3.



ligand and a proton which attacks the nucleophilic oxo ligand. Protonation of the NHC would leave the imidazolium cation and an electron-deficient compound of the type  $[\text{MoO}_2(\text{OH})\text{Cl}_2]^-$ , which may dimerize to yield  $[\text{MoO}_2(\text{OH})(\mu\text{-Cl})\text{Cl}]_2^{2-}$ . Dehydration of this latter complex would lead to the observed product  $[\text{Mo}_2(\mu\text{-O})(\mu\text{-Cl})_2\text{Cl}_2\text{O}_4]^{2-}$ . On the basis of this result, we examined the decomposition products of complexes **3** and **5**, and observed that their elemental analyses corresponded to complexes with the same composition as **6**, with the only difference of the nature of the counter-cations. This mechanism would also be operative for decomposition of the biscarbene-complexes **1** and **2**, through a mono-NHC complex (similar to **3–5**) formed by the decoordination of one NHC ligand. This decoordination of the NHC ligand was previously described by Herrmann and co-workers [7].

### Acknowledgements

The authors thank FCT, POCI and FEDER through project POCI/QUI/55586/2004, the Ministerio de Educación y Ciencia and CRUP (Ações Integradas Programme) for general support. We also gratefully acknowledge financial support from the MEC of Spain (projects CTQ2005-05187) and Bancaixa (P1.1B2004-07). We wish to acknowledge Maria da Conceição Almeida for providing data from the Elemental Analyses Service at the Instituto de Tecnologia Química e Biológica (ITQB), Universidade Nova de Lisboa, Oeiras, Portugal. P. M. Reis thanks FCT for a postdoctoral grant and E.M.-M thanks the Spanish Ministerio de Educación y Ciencia for a fellowship.

### Appendix A. Supplementary data

Molecular diagram, crystal data, structure refinement, bond lengths [Å] and angles [°] for compound **6** can be found as supplementary information. Copies of this information can be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>) by quoting the deposition number CCDC 292384. NMR spectra. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.02.004.

### References

[1] A.J. Arduengo, R.L. Harlow, M. Kline, *J. Am. Chem. Soc.* 113 (1991) 361.  
 [2] (a) W.A. Herrmann, C. Köcher, *Angew. Chem., Int. Edit.* 36 (1997) 2162;

(b) W.A. Herrmann, T. Weskamp, V.P.W. Böhm, *Adv. Organomet. Chem.* 48 (2001) 1;  
 (c) W.A. Herrmann, *Angew. Chem., Int. Edit.* 41 (2002) 1290;  
 (d) R.H. Crabtree, *Pure Appl. Chem.* 75 (2003) 435;  
 (e) E. Peris, R.H. Crabtree, *C. R. Chimie* 6 (2003) 33;  
 (f) E. Peris, R.H. Crabtree, *Coordin. Chem. Rev.* 248 (2004) 2239;  
 (g) D. Bourissou, O. Guerret, F.P. Gabbaï, G. Bertrand, *Chem. Rev.* 100 (2000) 39;  
 (h) C.M. Crudden, D.P. Allen, *Coordin. Chem. Rev.* 248 (2004) 2247.  
 [3] (a) N. Kühn, T. Kratz, D. Blaser, R. Boese, *Inorg. Chim. Acta* 238 (1995) 179;  
 (b) W.A. Herrmann, K. Öfele, M. Elison, F.E. Kühn, P.W. Roesky, *J. Organomet. Chem.* 480 (1994) C7;  
 (c) D.S. McGuinness, V.C. Gibson, J.W. Steed, *Organometallics* 23 (2004) 6288;  
 (d) C.D. Abernethy, G.M. Codd, M.D. Spicer, M.K. Taylor, *J. Am. Chem. Soc.* 125 (2003) 1128.  
 [4] H. Braband, T.I. Zahn, U. Abram, *Inorg. Chem.* 42 (2003) 6160.  
 [5] B. Royo, E. Herdtweck, C.C. Romão, *Eur. J. Inorg. Chem.* (2004) 3305.  
 [6] (a) K. Öfele, W.A. Herrmann, D. Mihališ, M. Elison, E. Herdtweck, T. Priermeier, P. Kiprof, *J. Organomet. Chem.* 498 (1995) 1;  
 (b) K. Öfele, W.A. Herrmann, D. Mihališ, M. Elison, E. Herdtweck, W. Scherer, J. Mink, *J. Organomet. Chem.* 459 (1993) 177.  
 [7] W.A. Herrmann, G.M. Lobmaier, M. Elison, *J. Organomet. Chem.* 520 (1996) 231.  
 [8] R. Colton, I.B. Tomkins, *Aust. J. Chem.* 18 (1965) 447.  
 [9] N. Kühn, T. Kratz, *Synthesis-Stuttgart* (1993) 561.  
 [10] W.A. Herrmann, C. Köcher, L.J. Goossen, G.R.J. Artus, *Chem. Eur. J.* 2 (1996) 1627.  
 [11] (a) S. Gago, J.E. Rodriguez-Borges, C. Teixeira, A.M. Santos, J. Zhao, M. Pillinger, C.D. Nunes, Z. Petrovski, T.M. Santos, F.E. Kühn, C.C. Romão, I.S. Goncalves, *J. Mol. Catal. A: Chem.* 236 (2005) 1;  
 (b) C.J. Doonan, A.J. Millar, D.J. Nielsen, C.G. Young, *Inorg. Chem.* 44 (2005) 4506;  
 (c) G. Wang, G. Chen, R.L. Luck, Z.Q. Wang, Z.C. Mu, D.G. Evans, X. Duan, *Inorg. Chim. Acta* 357 (2004) 3223;  
 (d) M.D. Brown, M.B. Hursthouse, W. Levason, R. Ratnani, G. Reid, *Dalton Trans.* (2004) 2487;  
 (e) M.B. Hursthouse, W. Levason, R. Ratnani, G. Red, *Polyhedron* 23 (2004) 1915;  
 (f) N. Manwani, M.C. Gupta, R. Ratnani, J.E. Drake, M.B. Hursthouse, M.E. Light, *Inorg. Chim. Acta* 357 (2004) 939;  
 (g) F.E. Kühn, A.M. Santos, A.D. Lopes, I.S. Goncalves, J.E. Rodriguez-Borges, M. Pillinger, C.C. Romão, *J. Organomet. Chem.* 621 (2001) 207;  
 (h) R.J. Butcher, B.R. Penfold, E. Sinn, *J. Chem. Soc., Dalton Trans.* (1979) 668.  
 [12] A.M. Magill, K.J. Cavell, B.F. Yates, *J. Am. Chem. Soc.* 126 (2004) 8717.  
 [13] H. Braband, T.I. Kückmann, U. Abram, *J. Organomet. Chem.* 690 (2005) 5421.  
 [14] (a) J.K. Huang, H.J. Schanz, E.D. Stevens, S.P. Nolan, *Organometallics* 18 (1999) 2370;  
 (b) W.J. Oldham, S.M. Oldham, B.L. Scott, K.D. Abney, W.H. Smith, D.A. Costa, *Chem. Commun.* (2001) 1348.  
 [15] T.I. Kückmann, U. Abram, *Inorg. Chem.* 43 (2004) 7068.  
 [16] M.D. Huang, C.W. Dekock, *Inorg. Chem.* 32 (1993) 2287.  
 [17] T. Ozeki, M. Sakaguchi, A. Yagasaki, *Polyhedron* 19 (2000) 43.