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Synthesis and characterization of oxo–imido and alkyl–imido complexes of molybdenum(VI)

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Abstract

Treatment of the complex Mo(Nmes)(O)Cl_2(dme) (mes = 2,4,6-trimethylphenyl; dme = 1,2-dimethoxyethane) with KTp^{Me2}, NaCp and bipy gives the corresponding derivatives (Tp^{Me2})Mo(Nmes)(O)Cl (**1**), CpMo(Nmes)(O)Cl (**2**) and Mo(Nmes)(O)Cl_2(bipy) (**3**). Other oxo–imido compounds of composition Mo(Nmes)(O)(S_2CNR_2)$_2$ ($R_2 = C_4H_4$ **4**, C_5H_{10} **5**, $^iPr_2$ **6**) can be obtained by reacting Mo(Nmes)(O)Cl_2(dme) with the appropriate dithiocarbamate salt. The NMR properties of **4**–**6** are consistent with the presence of two rapidly equilibrating dithiocarbamate ligands. The reaction of Mo(Nmes)(O)Cl_2(dme) with different Grignard reagents, Mg(R)X, produces the trialkyl imido complexes Mo(Nmes)R_3Cl (R = Me **7**, $CH_2C(Me)_2Ph$ **8**, CH_2SiMe_3 **9**).

Keywords: Imido; Oxo; Molybdenum; Alkyl

1. Introduction

Interest in the chemistry of transition metal compounds that contain multiple bonded ligands has increased greatly in the last decades [1], due mainly to their involvement in many important reactions. Of particular importance are the high-valent organo-imido and -oxo molybdenum derivatives, which have been subjected to intense investigations. A large number of bis(imido) [2] and dioxo complexes [3] of this metal are known, but information on the related mixed-terminal oxo–imido compounds is still scarce [4]. We have recently shown [5] that the compound Mo(Nmes)(O)Cl_2(dme) (mes = 2,4,6-trimethylphenyl; dme = 1,2-dimethoxyethane) can be prepared from Mo(Nmes)$_2Cl_2$(dme) and Mo(O)$_2Cl_2$(dme). As an extension of this work [6], we describe here the synthesis and characterization of several oxo–imido complexes of molybdenum that contain Tp^{Me2} (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate), C_5H_5 (Cp), 2,2′-bipyridine (bipy) and dithiocarbamate ligands, as well as that of trialkyl imido compounds of formula Mo(Nmes)R_3Cl. As discussed below, these new imido species have been prepared using the complex Mo(Nmes)(O)Cl_2(dme) as the starting material.

2. Experimental

All preparations and other operations were carried out under a dry, oxygen-free, nitrogen atmosphere, following conventional Schlenk techniques. Solvents were dried and degassed before use. Microanalyses were carried out by the Microanalytical Service of the IIQ (Seville). Infrared spectra were recorded on Perkin–Elmer model 883 spectrophotometer. ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were run on Bruker AMX-300 and Bruker AMX-500 spectrometers. ^{31}P shifts were measured with respect to external 85% H_3PO_4. ^{13}C-NMR spectra were referenced using the ^{13}C resonance of the solvent as an internal standard but are reported with respect to $SiMe_4$. The petroleum ether used had b.p. 40–60°C. Compound $MoCl_2$(Nmes)(O)(dme) was prepared according to the literature procedure [5].

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2.1. Preparation of $Tp^{Me2}Mo(Nmes)(O)Cl$ (1)

A mixture of $MoCl_2(Nmes)(O)(dme)$ (0.1 g, 0.25 mmol) and KTp^{Me2} (0.08 g, 0.25 mmol) was dissolved in THF (25 ml) and stirred at room temperature (r.t.) overnight. The solvent was removed under vacuum and the solid extracted with a 1:1 Et_2O–petroleum ether mixture. The solution was concentrated and cooled at −20°C. Compound **1** was isolated as a purple solid (0.07 g, 48% yield). ^{1}H-NMR (500 MHz, C_6D_6): δ 6.63, 6.39 (s, 1, CH, Ph), 5.55, 5.52, 5.32 (s, 1, CH, Tp^{Me2}), 3.39, 3.15, 2.59, 2.32, 2.09, 2.06, 2.03, 1.97, 1.73 (s, 3, CH_3). $^{13}C\{^1H\}$-NMR (75 MHz, C_6D_6): δ 153.5, 153.3, 153.1, 153.0, 145.3, 143.2, 142.6, 141.2, 138.1, 133.5 (C, Tp^{Me2} and Ph), 129.0, 127.8 (*m*-C), 107.0, 106.7, 106.5 (CH, Tp^{Me2}), 20.7, 18.5, 16.9, 15.1, 14.6, 14.3, 12.4, 12.0, 11.9 (CH_3, Tp^{Me2}, *p*- and *o*-CH_3). Anal. Calc. for $C_{24}H_{33}N_7BClMoO$ 1/4 Et_2O: C, 50.4; H, 6.0; N, 16.5. Found: C, 50.5; H, 5.9; N, 16.5.

2.2. Preparation of CpMo(Nmes)(O)Cl (2)

To a solution of $MoCl_2(Nmes)(O)(dme)$ (0.18 g, 0.44 mmol) in THF (30 ml) was added one equivalent of NaCp (0.67 M solution in THF) and the mixture stirred at r.t. overnight. The solvent was removed in vacuum and Et_2O (30 ml) was added to dissolve the resulting green solid. The suspension was filtered and the solution concentrated and cooled at −20°C. Compound **2** was obtained as an orange crystalline solid (0.05 g, 33% yield). ^{1}H-NMR (300 MHz, C_6D_6): δ 6.56 (s, 2, CH, Ph), 5.83 (s, 5, CH, Cp), 2.50 (s, 6, *o*-CH_3), 2.07 (s, 3, *p*-CH_3). $^{13}C\{^1H\}$-NMR (75 MHz, C_6D_6): δ 154.7 (C *ipso*), 139.1, 138.2 (*p*- and *o*-C), 128.7 (*m*-C), 111.2 (Cp), 21.3 (*p*-CH_3), 18.7 (*o*-CH_3). Anal. Calc. for $C_{14}H_{16}NClMoO$: C, 48.6; H, 4.6; N, 4.0. Found: C, 47.6; H, 4.5; N, 4.0.

2.3. Preparation of $MoCl_2(Nmes)(O)(bipy)$ (3)

A solution of $MoCl_2(Nmes)(O)(dme)$ (0.1 g, 0.25 mmol) in Et_2O (20 ml) was treated with a solution of bipy (0.04 g, 0.25 mmol) in Et_2O (15 ml). A red solid was formed immediately, which was collected by filtration, washed with Et_2O and extracted with hot toluene (90°C). The resulting solution was cooled to r.t. and compound **3** was obtained as a red crystalline solid (0.09 g, 76% yield). ^{1}H-NMR (300 MHz, acetone-d_6): δ 9.77, 9.28 (m, 1, bipy), 8.68, 8.35 (m, 2, bipy), 7.96, 7.84 (m, 1, bipy), 6.93 (s, 2, CH, Ph), 2.83 (s, 6, *o*-CH_3), 2.34 (s, 3, *p*-CH_3). $^{13}C\{^1H\}$-NMR (75 MHz, acetone-d_6): δ 153.0, 152.3 (C *ipso*, bipy), 150.9 (C *ipso*, Ph), 142.0, 141.6 (C, bipy), 139.2, 137.4 (*p*- and *o*-C), 129.3 (*m*-C), 127.55, 127.5, 124.4 (C, bipy), 21.1 (*p*-CH_3), 19.0 (*o*-CH_3). Anal. Calc. for $C_{19}H_{19}N_3Cl_2MoO$: C, 48.3; H, 4.0; N, 8.9. Found: C, 49.1; H, 3.9; N, 8.3.

2.4. Synthesis of $Mo(Nmes)(O)(S_2CNR_2)_2$ ($R_2 = C_4H_4$ 4, C_5H_{10} 5, $^iPr_2$ 6) complexes

A mixture of $MoCl_2(Nmes)(O)(dme)$ (0.20 g, 0.49 mmol) and $KS_2CNC_4H_4$ (0.20 g, 1.1 mmol) was dissolved in THF (25 ml). The solution was stirred at r.t. overnight. The solvent was then removed and the resulting solid recrystallized from a Et_2O–petroleum ether mixture. Compound **4** was collected as orange crystals (0.16 g, 61% yield). ^{1}H-NMR (300 MHz, C_6D_6): δ 7.35 (pt, 2.3 Hz, 4, pyrrole), 6.53 (s, 2, CH, Ph), 5.89 (pt, 2.3 Hz, 4, pyrrole), 2.85 (s, 6, *o*-CH_3), 2.04 (s, 3, *p*-CH_3). $^{13}C\{^1H\}$-NMR (75 MHz, C_6D_6): δ 210.9 (CS_2), 154.6 (C *ipso*), 142.0, 141.5 (*p*- and *o*-C), 128.5 (*m*-C), 119.4, 115.7 (CH, pyrrole), 21.1 (*p*-CH_3), 19.3 (*o*-CH_3). Anal. Calc. for $C_{19}H_{19}N_3MoOS_4$: C, 43.1; H, 3.6; N, 7.9. Found: C, 43.1; H, 3.6; N, 8.0.

Compounds **5** and **6** were obtained as red and orange crystals in 50 and 35% yield, following the procedure described for **4**, but using $NaS_2CNC_5H_{10}$ and $NaS_2CN^iPr_2$, respectively. $Mo(Nmes)(O)(S_2CNC_5H_{10})_2$ (**5**): ^{1}H-NMR (300 MHz, C_6D_6): δ 6.58 (s, 2, CH, Ph), 3.38 (br, 8, CH_2), 3.09 (s, 6, *o*-CH_3), 2.01 (s, 3, *p*-CH_3), 0.90 (br, 12, CH_2). $^{13}C\{^1H\}$-NMR (75 MHz, C_6D_6): δ 199.9 (CS_2), 154.3 (C *ipso*), 140.2, 138.5 (*p*- and *o*-C), 128.2 (*m*-C), 49.1, 24.9 (4 CH_2), 23.2 (2 CH_2), 20.9 (*p*-CH_3), 19.6 (*o*-CH_3). Anal. Calc. for $C_{21}H_{31}N_3MoOS_4$ 1/4 Et_2O: C, 45.2; H, 5.7; N, 7.2. Found: C, 45.7; H, 5.8; N, 7.0. ^{1}H-NMR (300 MHz, 213 K, toluene-d_8): δ 6.45 (s, 2, CH, Ph), 3.6 (br m, 4, CH_2), 3.07 (s, 6, *o*-CH_3), 3.0 (br m, 4, CH_2), 1.99 (s, 3, *p*-CH_3), 0.83 (br, 12, CH_2). $^{13}C\{^1H\}$-NMR (75 MHz, 213 K, toluene-d_8): δ 199.4 (CS_2), 198.0 (CS_2), 154.6 (C ipso), 141.2, 139.3 (*p*- and *o*-C), 49.9, 49.4, 48.9 (br, CH_2), 25.2 (br, 4 CH_2), 23.6 (br, 2 CH_2), 21.6 (*p*-CH_3), 20.4 (*o*-CH_3), *m*-C is obscured by toluene-d_8. $Mo(Nmes)(O)(S_2CN^iPr_2)_2$ (**6**): ^{1}H-NMR (300 MHz, 298 K, C_6D_6): δ 6.58 (s, 2, CH, Ph), 3.04 (s, 6, *o*-CH_3), 2.02 (s, 3, *p*-CH_3), 0.95 (br, 4, CH_3). $^{13}C\{^1H\}$-NMR (75 MHz, C_6D_6): δ 201.0 (CS_2), 198.3 (CS_2), 154.2 (C *ipso*), 139.8, 138.0 (*p*- and *o*-C), 128.2 (*m*-C), 52.1 (br, CH), 20.9 (*p*-CH_3), 19.5 (*o*-CH_3), 19.3 (br, CH_3). ^{1}H-NMR (300 MHz, 340 K, C_6D_6): δ 6.62 (s, 2, CH, Ph), 4.37 (br, 1, CH), 4.20 (br, 1, CH), 2.98 (s, 6, *o*-CH_3), 2.05 (s, 3, *p*-CH_3), 1.06 (d, 6 Hz, 6, CH_3), 0.97 (d, 6 Hz, 6, CH_3).

2.5. Preparation of alkyl imido $Mo(Nmes)R_3Cl$ ($R = Me$ 7, $CH_2C(Me)_2Ph$ 8, CH_2SiMe_3 9) complexes

A solution of $MoCl_2(Nmes)(O)(dme)$ (0.2 g, 0.49 mmol) in Et_2O (40 ml) was treated, at −60°C, with three equivalents of Mg(Me)I (0.5 M solution in Et_2O). The mixture was allowed to warm to r.t. and the stirring was continued for 3 h. Filtration and evaporation of the volatiles under vacuum gave compound **7** as an orange oil (0.09 g, 60% yield). ^{1}H-NMR (500 MHz,

C_6D_6): δ 6.41 (s, 2, CH, Ph), 2.02 (s, 6, *o*-CH_3), 1.94 (s, 3, *p*-CH_3), 1.78 (s, 9, CH_3). $^{13}C\{^1H\}$-NMR (125 MHz, C_6D_6): δ 150.7 (C *ipso*), 140.5, 140.0 (*p*- and *o*-C), 129.2 (*m*-C), 52.6 (CH_3), 21.0 (*p*-CH_3), 19.3 (*o*-CH_3).

The use of similar procedures, but using three equivalents of $Mg(CH_2CMe_2Ph)Cl$ (0.87 M solution in Et_2O) and of $Mg(CH_2SiMe_3)Cl$ (1.4 M solution in Et_2O), allowed the preparation of compounds **8** and **9**, respectively. They were also obtained as orange oils (60% yield). This makes difficult to obtain reliable analytical data but they were fully characterized by solution NMR. Spectroscopic data for Mo(Nmes)($CH_2CMe_2Ph)_3Cl$ (**8**): ^{1}H-NMR (300 MHz, C_6D_6): δ 7.33–7.01 (m, 15, CH_2CMe_2*Ph*), 6.43 (s, 2, CH, Ph), 1.50 (s, 3, *p*-CH_3), 1.39 (s, 6, *o*-CH_3), 1.21 (s, 6, C*H*$_2$CMe$_2$Ph), 1.12 (s, 18, CH_2CMe_2Ph). $^{13}C\{^1H\}$-NMR (75 MHz, C_6D_6): δ 151.3 (C *ipso*), 150.7, 149.0 (CH_2CMe_2*Ph*), 140.2 (C, Ph), 129.2 (*m*-C), 87.6 (*C*H$_2$CMe$_2$Ph), 37.2 (CH_2*C*Me$_2$Ph), 31.7 (*p*-CH_3), 30.5 (*o*-CH_3), 28.9 (CH_2CMe_2Ph). Spectroscopic data for Mo(Nmes)-($CH_2SiMe_3)_3Cl$ (**9**): ^{1}H-NMR (300 MHz, C_6D_6): δ 6.56 (s, 2, CH, Ph), 2.58 (s, 6, C*H*$_2$Si(CH$_3$)$_3$), 2.50 (s, 6, *o*-CH_3), 2.03 (s, 3, *p*-C*H*$_3$), 0.23 (s, 27, $CH_2Si(CH_3)_3$). $^{13}C\{^1H\}$-NMR (75 MHz, C_6D_6): δ 148.3 (C *ipso*), 140.2, 138.1 (*p*- and *o*-C), 129.5 (*m*-C), 66.2 (*C*H$_2$Si(CH$_3$)$_3$), 20.3 (*p*-CH_3), 20.1 (*o*-CH_3), 1.6 ($CH_2Si(CH_3)_3$).

3. Results and discussion

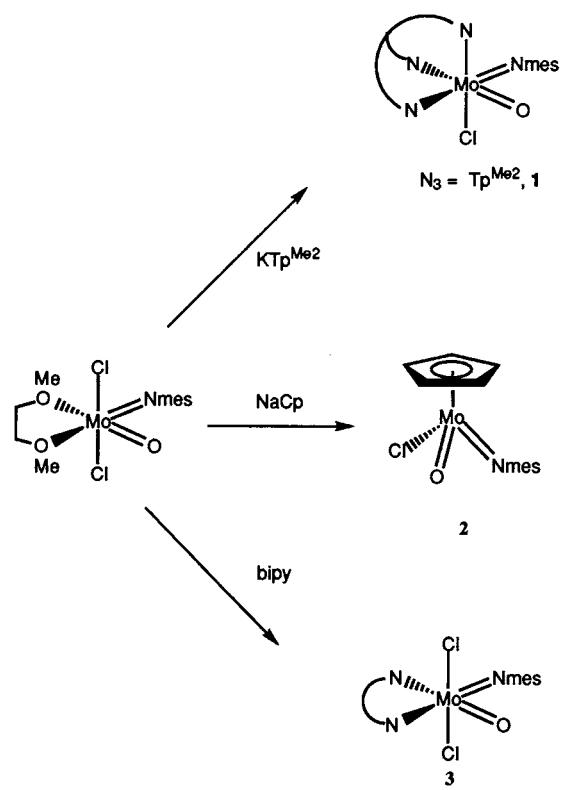
3.1. Synthesis and characterization of oxo–imido molybdenum(VI) complexes

We have recently reported [5] that the treatment of $Mo(Nmes)_2Cl_2(dme)$ with $Mo(O)_2Cl_2(dme)$ gives the complex $Mo(Nmes)(O)Cl_2(dme)$. This synthetic methodology constitutes a suitable entry to the chemistry of oxo–imido derivatives of molybdenum. Thus, the reaction of $Mo(Nmes)(O)Cl_2(dme)$ with one molar equivalent of KTp^{Me2} or NaCp leads to the formation of the complexes (Tp^{Me2})Mo(Nmes)(O)Cl (**1**) and Cp-Mo(Nmes)(O)Cl (**2**), respectively (Scheme 1). Analytical and NMR data are consistent with the proposed formulation. Related tris(pyrazolyl)borate [4a,f,5] and cyclopentadienyl [4h,5,7] oxo–imido derivatives of molybdenum and tungsten(VI) have been reported previously.

The facility with which the arylimido ligand of these compounds rotates around the nitrogen–carbon bond can be deduced from spectroscopic data. For complex **2**, free rotation around the M–C bond takes place in solution since only two methyl and one aromatic C–H resonances are observed in the ^{1}H-NMR spectrum (δ 2.07 *p*-CH_3, 2.50 *o*-CH_3, 6.56 *m*-H; relative intensities: 3:6:2). In contrast, the ^{1}H-NMR spectrum of **1** displays, at room temperature, nine signals for the methyl groups (six due to the Tp^{Me2} ligand and three for the *ortho* and *para* methyl groups of the aromatic ring). Two signals are additionally observed for the *meta* hydrogens. These data are in agreement with the absence of rotation of the aryl ring. Restricted rotation of the arylimido group has been reported in other systems [4d, 6a, 8] and it is generally attributed to steric factors. In our case, the presence of the bulky Tp^{Me2} ligand causes a steric congestion that hinders the rotation. In comparison, free rotation of the aryl imido ligand has been observed [5] in complex TpMo(Nmes)(O)Cl. This is in agreement with the differences in the cone angles reported [9] for these ligands (199°, Tp; 236°, Tp^{Me2}).

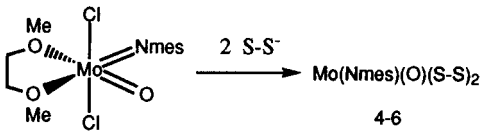
Addition of one equivalent of bipy to a solution of $Mo(Nmes)(O)Cl_2(dme)$ in Et_2O produces the complex $MoCl_2(Nmes)(O)(bipy)$ (**3**) by substitution of the coordinated dme. This compound is obtained as a red crystalline solid from hot toluene solutions. The NMR data are in agreement with the structure represented in Scheme 1. The ^{1}H-NMR spectrum is consistent with a 1:1 ratio of the organoimido and bipy ligands. The related tungsten compound, $W(N^tBu)(O)Cl_2(bipy)$, is known [10] and has been structurally characterized by X-ray crystallography.

The reaction of $MoCl_2(Nmes)(O)(dme)$ with two equivalents of the potassium 1-pyrrole-carbodithioate, $KS_2CNC_4H_4$, sodium 1-piperidine-carbodithioate,



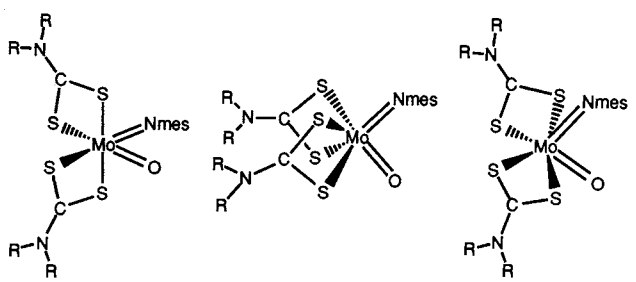
Scheme 1.

$NaS_2CNC_5H_{10}$, or sodium diisopropyldithiocarbamate, $NaS_2CN^iPr_2$, in THF gives the complexes Mo(Nmes)(O)$(S_2CNR_2)_2$ ($R_2 = C_4H_4$ **4**, C_5H_{10} **5**, $^iPr_2$ **6**) (Eq. (1)).



(1)

Analytical data are consistent with the proposed formulation but the NMR features of these complexes are unexpected. Thus, for compounds **4** and **5**, ^{1}H- and $^{13}C\{^1H\}$-NMR data are in agreement with the presence of two equivalent dithiocarbamate ligands. Similar ^{1}H-NMR characteristics have been reported for other oxo–imido complexes Mo(NR)(O)$(S_2CNEt_2)_2$ [4i,j], and oxo–hydrazido(2-) complexes Mo(NNR_2)(O)-$(S_2CNR'_2)_2$ [11], but no attempts have been made to investigate their solution dynamics. The room temperature ^{1}H-NMR spectrum of **4**, recorded in benzene-d_6 displays two pseudo-triplets (δ 7.35 and 5.89) each for four hydrogen nuclei of the pyrrole fragment. Furthermore, the $^{13}C\{^1H\}$-NMR spectrum shows two sharp signals in the pyrrole region (δ 119.4 and 115.7) and only one resonance for the two S_2C units (δ 210.9). In the case of complex **5**, the $^{13}C\{^1H\}$-NMR spectrum shows again only one resonance for the two S_2C fragments (δ 199.9). A rigid distorted octahedral structure, with a *cis* distribution of the two multiple bonded ligands [4i], (see **I**) cannot account for these observations.

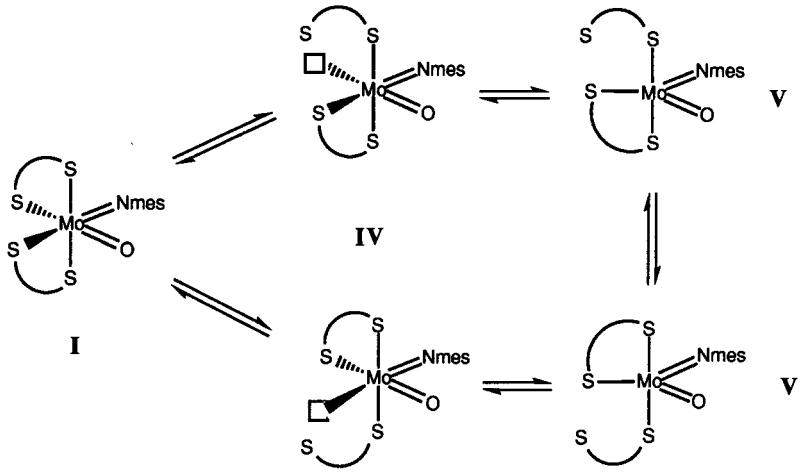


Other coordination geometries, such as trigonal prism **II** or skew–trapezoidal–bipyramidal **III** could account for the NMR properties of **4** and **5**. It should be noted, however, that whilst structure type **III** has been reported for some dioxo compounds [12], as far as we are aware the structure **II** has no precedent in complexes of this kind and it is electronically less favorable than the octahedral geometry [13]. Since in addition compound **6** exhibits detectable fluxional behavior in solution it is reasonable to assume that a dynamic process is responsible for the NMR properties of **4** and **5**. At variance with the data already described for these two compounds, the $^{13}C\{^1H\}$-NMR spectrum of **6**, recorded at 25°C, shows two resonances (δ 201.0, 198.3 ppm) for the S_2C groups, in accord with the presence of two inequivalent dithiocarbamate ligands. At the same temperature, the ^{1}H-NMR spectrum displays a broad signal (δ 0.95) for the methyl groups of the ^{i}Pr units. Moreover, the CH group resonances of the four isopropyl units cannot be discerned. Upon increasing the temperature (340 K), a broad hump centered at 4.37 ppm, attributable to the CH groups is observed. A similar situation is found when variable temperature NMR studies of the analogous compound **5** are undertaken. Relevant information is provided by the $^{13}C\{^1H\}$-NMR spectra. At 213 K, two S_2C carbon resonances, centered at 199.4 and 198.0 ppm, and several broad signals due to the CH_2 groups bonded to the nitrogen atom of the piperidine fragments are observed. The splitting clearly indicates the existence of non-equivalent dithiocarbamate ligands, the low-temperature spectrum actually being consistent with the octahedral structure **I**. The magnetic equivalence of the two dithiocarbamate ligands, at the fast interchange limit, may then be proposed to be due to the mechanistic path depicted in Scheme 2.

Considering the strong *trans* influence exerted by the oxo and imido ligands and assuming that their *trans* effect follows the same trend, a facile dissociation of the sulfur atoms occupying the *trans* position with respect to these oxo and imido functionalities is likely to occur in solution. This process would create a vacant coordination position (**IV**) and the adoption of a five-coordinate configuration (**V**) containing (*S*,*S*′)-S_2CNR_2 and (*S*)-S_2CNR_2 ligands. A fast concerted exchange of the mono- and the bidentate dithiocarbamate ligands renders these groups equivalent. A similar equilibration of the two dithiocarbamate units has been observed in the $^{13}C\{^1H\}$-NMR spectra of Pt((*S*,*S*′)-S_2CNR_2)((*S*)-S_2CNR_2)(PR_3) complexes, at room temperature [14] and an analogous explanation, based on mono- and bidentate ligand exchange through five-coordinated species, has been proposed to account for their dynamic NMR behavior. Moreover, interconversion of monodentate and bidentate coordination modes have also been noticed in square-planar gold-dithiocarbamate compounds [15,16] and in complexes of *O*-alkyldithiocarbonate (xanthate) ligands [17]. Nevertheless, a mechanism involving the equilibration of the ligands through structures of type **II** or **III** can not be excluded on the basis of the NMR data.

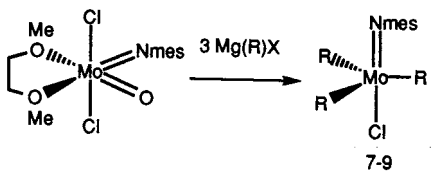
3.2. Synthesis of trialkyl imido molybdenum(VI) complexes

The reaction of the complex Mo(Nmes)$(O)Cl_2$(dme) with three equivalents of the Grignard reagents Mg(Me)I, $Mg(CH_2C(Me)_2Ph)Cl$, and $Mg(CH_2SiMe_3)Cl$ produces the alkyl compounds Mo(Nmes)R_3Cl (R =



Scheme 2.

Me **7**, $CH_2C(Me)_2Ph$ **8**, CH_2SiMe_3 **9**) (Eq. (2)).



(2)

As is evident from the composition of compounds **7**–**9**, their formation requires the abstraction of the oxo and one of the chloride ligands from the coordination sphere of the metal. Similar synthetic methodology was employed previously by Osborn and co-workers [18], using dialkylmagnesium reagents. Derivatives **7**–**9** are orange oils, very soluble in hydrocarbon solvents. The C_{3v} symmetry [12,19] proposed for these molecules is readily apparent from the NMR data. For instance, the ^1H- and $^{13}C\{^1H\}$-NMR spectra of **7** show only one resonance for the three methyl groups (^1H-NMR: δ 1.78; $^{13}C\{^1H\}$-NMR: δ 52.6 ppm). For the complexes **8** and **9** one signal due to the three methylene groups of the CH_2R alkyl ligands is also observed (^1H-NMR: δ 1.21, **8**; 2.58, **9**; $^{13}C\{^1H\}$ NMR: δ 87.6, **8**; 66.2 ppm, **9**). Analogous trialkyl imido complexes of tungsten were reported earlier by Pedersen and Schrock [20] and, very recently, Royo and co-workers have characterized related trialkyl imido cyclopentadienyl complexes of tungsten [21].

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