

The Amido and Bisalkoxo-Complexes of [Tri(3,5-Dimethylpyrazolyl)Borato]Molybdenum Nitrosyl

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In this study, the amido nitrosyl molybdenum complex, $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{NH}_2)]$, was prepared. This compound reacts with alcohols, yielding the bisalkoxo complexes, $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})(\text{OR})_2]$ ($\text{R} = \text{Me}, \text{Et}, \text{Pr}^n, \text{Bu}^n$). The new complexes were analyzed by IR and $^1\text{H-NMR}$ spectroscopy.

Introduction

The hydrotris(pyrazol-1-yl)borate ligand, $[\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}]^-$, has been likened to cyclopentadienide C_5H_5^- , as both are uninegative, with electron donors which can occupy three facial co-ordination sites on a metal ion¹.

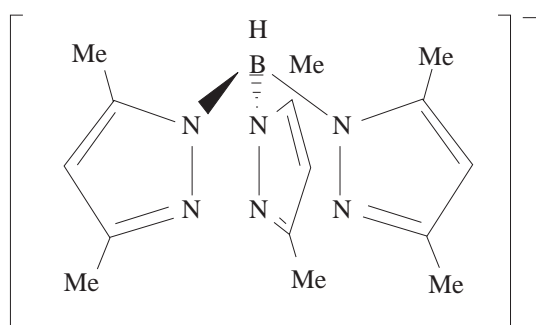


Figure 1. The structural formula² of $[\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}]^-$

It is known¹ that complexes containing hydrotris(pyrazol-1-yl)borate tend to be more stable and less reactive than their counterpart containing C_5H_5 . In part, this may be attributed to the more sterically demanding nature of hydrotris(pyrazol-1-yl)borate, at least in the region of the pyrazole rings³. Compounds containing the sterically-hindered tris(3,5-dimethylpyrazolyl)borate molybdenum nitrosyl group $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})]^{2+}$ have found applications as Group I cation sensors⁴, as components

of materials having non-linear optical properties^{5,6} and as precursors for oligonuclear compounds exhibiting novel magnetic behaviour⁷. It has been suggested⁸ that such a range of applications depends on the particular and unique combination of factors associated with molybdenumtris(pyrazol-1-yl)borato nitrosyl functionality.

It has been shown⁹ that there are strong analogies between the behaviour of metal complexes containing hydrotris(pyrazol-1-yl)borate anions and those containing the η^5 -cyclopentadienyl ligand. Thus $[\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}]$ reacts^{10,11} with $[\text{Mo}(\text{CO})_6]$ affording the carbonylate ion, $[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{CO})_3]^-$, the chemistry which is very similar to that of $[\text{Mo}\{\eta^5\text{-C}_5\text{H}_5\}(\text{CO})_3]^-$. Indeed, acidification followed by nitrosylation of the pyrazolylborate complex yielded $[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})(\text{CO})_2]$ in a way entirely similar to the preparation of $[\text{Mo}\{\eta^5\text{-C}_5\text{H}_5\}(\text{NO})(\text{CO})_2]$.

McCleverty *et al.*¹² discovered that at room temperature, halogenation of the compounds $[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})(\text{CO})_2]$ ($\text{R} = \text{H}$ or Me) in CCl_4 ($\text{X} = \text{Cl}$ or Br) or hexane ($\text{X} = \text{I}$) yielded $[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{X}_2]_n$ ($\text{R} = \text{H}$, $n = 2$; $\text{R} = \text{Me}$, $n = 1$). They suggested¹² that the reaction stoichiometry was strictly adhered to; indeed the reaction of $[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})(\text{CO})_2]$ with an excess of X_2 ($\text{X} = \text{Cl}$ or Br) yielded $[\text{Mo}\{\text{HB}(3,5\text{-Me}_2\text{-4-X-C}_3\text{N}_2)_3\}(\text{NO})\text{X}_2]$. The compound $[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})(\text{CO})_2]$ with iodine and benzyl chloride in toluene¹³.

Mono amido species, $[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{I}(\text{Y})]$ ($\text{Y} = \text{NMe}_3$ or HNR , where $\text{R} = \text{H}$, Me , Et , Pr^n , Pr^i , Bu^n , Bu^t , C_6H_{11} , C_3H_5 or CH_2Ph) have been prepared¹⁴ by treatment of the species where $\text{Y} = \text{I}$ with an excess of ammonia and primary amines. These compounds were reported¹¹ to be air- and moisture-stable, and could be kept as solids in open containers for several weeks.

Monoalkoxo complexes, $[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{X}(\text{Y})]$, ($\text{X} = \text{Cl}$, Br , I ; $\text{Y} = \text{OR}$. Where $\text{R} = \text{Me}$, Et , Pr^i , Bu^i , C_3H_5), have been prepared¹² by the reaction of the dihalogen compound, $[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{X}_2]$ ($\text{X} = \text{Cl}$, Br or I) with the appropriate alcohol. These six coordinate compounds were reported to be air- and moisture-stable¹⁵.

McCleverty *et al.*¹⁵ prepared bisalkoxo- and mixed alkoxo-complexes of tris (3,5-dimethylpyrazol)boratomolybdenum, $[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{X}(\text{Y})]$ [$\text{X} = \text{I}$, $\text{Y} = \text{OH}$, OC_6H_{11} and $\text{OCH}_2\text{CH}_2\text{CH}_2\text{OH}$; $\text{X} = \text{Y} = \text{OR}$ ($\text{R} = \text{H}$, Me , Et , Pr^i , Bu^i); $\text{X} = \text{OEt}$, $\text{Y} = \text{OPr}^i$, $\text{Y} = \text{OBu}^i$, $\text{X} = \text{OR}$, $\text{Y} = \text{HNR}'$ ($\text{R} = \text{Me}$, $\text{R}' = \text{H}$, Me and Et ; $\text{R} = \text{Et}$, $\text{R}' = \text{H}$, Me , Et , Pr^n , C_6H_{11} , and CH_2Ph ; $\text{R} = \text{Pr}^i$, $\text{R}' = \text{H}$, Me , Et , Pr^i , and C_6H_{11})]. The structure of the complexes $[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})(\text{OR})(\text{OR}')]$ ($\text{R} = \text{R}' = \text{Et}$ or Pr^i ; $\text{R} = \text{Et}$, $\text{R}' = \text{OPr}^i$) have been determined¹⁵ crystallographically. The molecules were reported to be six co-ordinate, with linear $\text{Mo}-\text{N}-\text{O}$ groups and short $\text{Mo}-\text{O}$ bond lengths (1.90Å).

In this study, the synthesis of the amido species, $[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{NH}_2)]$ and its reaction with alcohols, ROH ($\text{R} = \text{Me}$, Et , Pr^n , Bu^n) were investigated.

Experimental

$[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cy}_2]$ was prepared as described in the literature¹³. All other reagents were used as purchased without further purification. Solvents were rigorously dried before use. All yields are based on the starting metal-containing compound.

¹H NMR spectra were recorded on a JEOL GX270 instrument. IR spectra were measured using a PE 1600 FTIR spectrophotometer. Micro analyses were carried out by the Microanalytical Laboratory of the School of Chemistry at the University of Bristol.

Preparation of [Mo{HM(3, 5 – Me₂C₃HN₂)₃}(NO)Cl(NH₂)]

A solution of the compound [Mo{HM(3, 5 – Me₂C₃HN₂)₃}(NO)Cl₂] (0.20 g, 0.40 mmol) and an excess of ammonia solution (d 0.88; 2 mL) in toluene room temperature was stirred for two hours, during which time an orange precipitate formed. The solution was filtered, and the residue was washed with hexane and recrystallised from dichloromethane-hexane, yielding the desired product, orange microcrystals of [Mo{HM(3, 5 – Me₂C₃HN₂)₃}(NO)Cl(NH₂)], yield 0.16 g (86%).

Preparation of [Mo{HM(3, 5 – Me₂C₃HN₂)₃}(NO)(OMe)₂]

A mixture of [Mo{HM(3, 5 – Me₂C₃HN₂)₃}(NO)Cl(NH₂)] (0.2, 0.42 mmol) and methanol (20 mL) was refluxed for six hours in the presence of triethylamine (2-3 drops). The solution was cooled and the alcohol was removed *in vacuo*. Recrystallisation from dichloromethane-hexane (1:4) afforded the desired product, pink microcrystals of [Mo{HM(3, 5 – Me₂C₃HN₂)₃}(NO)(OMe)₂], yield 0.15 g (72%).

Preparation of [Mo{HM(3, 5 – Me₂C₃HN₂)₃}(NO)(OEt)₂]

The preparation of this complex was similar to that of [Mo{HM(3, 5 – Me₂C₃HN₂)₃}(NO)(OMe)₂] except that ethanol (20 mL) was used. The desired product [Mo{HM(3, 5 – Me₂C₃HN₂)₃}(NO)(OEt)₂] was isolated as pink microcrystals, yield 0.17 g (76%).

Preparation of [Mo{HM(3, 5 – Me₂C₃HN₂)₃}(NO)(OPrⁿ)₂]

The preparation of this complex was similar to that of [Mo{HM(3, 5 – Me₂C₃HN₂)₃}(NO)(OMe)₂] except that n-propanol (20 mL) was used. The desired product [Mo{HM(3, 5 – Me₂C₃HN₂)₃}(NO)(OPrⁿ)₂] was isolated as pink microcrystals, yield, 0.16 g (70%).

Preparation of [Mo{HM(3, 5 – Me₂C₃HN₂)₃}(NO)(n-Buc)₂]

The preparation of this complex was similar to that of [Mo{HM(3, 5 – Me₂C₃HN₂)₃}(NO)(OMe)₂] except that n-butanol (20 mL) was used. The desired product [Mo{HM(3, 5 – Me₂C₃HN₂)₃}(NO)(OBu₂)₂] was isolated as pink microcrystals, yield 0.16 g (68%).

Results and Discussion**Synthetic Studies**

The reaction of the compound, [Mo{HM(3, 5 – Me₂C₃HN₂)₃}(NO)Cl₂] with an excess of ammonia in toluene at room temperature afforded the orange complex, [Mo{HM(3, 5 – Me₂C₃HN₂)₃}(NO)Cl(NH₂)] (Figure 2). As mentioned above, the orange compounds, [Mo{HM(3, 5 – Me₂C₃HN₂)₃}(NO)X(NH₂)] (X = Br or I), were obtained¹⁴ by treating the appropriate dihalogen complex [Mo{HM(3, 5 – Me₂C₃HN₂)₃}(NO)X₂] with an excess of ammonia.

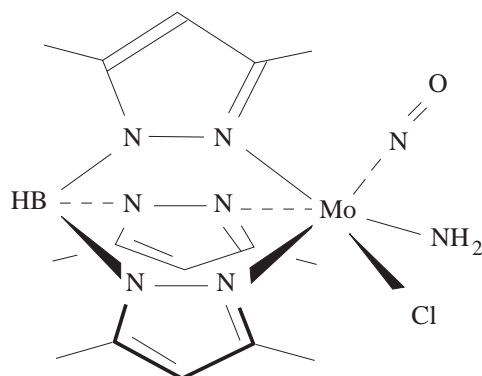


Figure 2. The structural formula of the compound $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{NH}_2)]$

Reactions of the amido complex, $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{NH}_2)]$ with alcohols ROH ($\text{R} = \text{Me}, \text{Et}, \text{Pr}^n, \text{Bu}^n$) in the presence of triethylamine were carried out in an attempt to obtain the monoalkoxo-complexes. In this reaction, triethylamine was used to facilitate elimination of HCl from the reaction system. Surprisingly, the pink microcrystals obtained from all four reactions suggested a bisalkoxo-type compound, as the known¹⁵ compounds $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})(\text{OR})_2]$ ($\text{R} = \text{Me}$ and Et) are pink by the reaction of $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{I}(\text{OR})]$ with silver acetate in an ROH-methylcyclohexane mixture. Moreover, the monoalkoxo-compounds, $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})(\text{NH}_2)(\text{OR})]$ ($\text{R} = \text{Me}$ or Et), have been synthesised by treating $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{I}(\text{OR})]$ with ammonia as orange microcrystals¹⁵.

During the reaction of the amido complex $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{NH}_2)]$ with ROH ($\text{R} = \text{Me}, \text{Et}, \text{Pr}^n, \text{Bu}^n$) in the presence of triethylamine, HCl was produced as a result of chloride abstraction. It is known¹⁵ that treatment of $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{X}(\text{Y})]$ ($\text{X} = \text{I}, \text{Y} = \text{OR}; \text{X} = \text{OR}, \text{Y} = \text{OR}'$; $\text{X} = \text{OR}, \text{Y} = \text{NHR}'$; where R and R' are both an alkyl) with HCl causes cleavage of the M–O and M–N bonds and formation of $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{X}(\text{Y})]$ ($\text{X} = \text{I}, \text{Y} = \text{Cl}; \text{X} = \text{Y} = \text{Cl}$). During the reaction of $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{NH}_2)]$ with the alcohols ROH ($\text{R} = \text{Me}, \text{Et}, \text{Pr}^n, \text{Bu}^n$) in the presence of triethylamine, it is possible that the monoalkoxo-complexes $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})(\text{NH}_2)(\text{OR})]$ are formed at first. Mo–N and M–O bond cleavage induced by HCl would then lead to formation of the dihalogen species $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{X}_2]$ ($\text{x} = \text{Cl}, \text{Br}$ or I) according to the reaction mentioned above. These coordinatively unsaturated (16e) transient species are known¹⁶ as redox-active and much of their substitution chemistry appears to involve redox reactions arising from prior dissociation of X^- , which would then act as a reducing agent for the parent dihalogen, giving the paramagnetic (17e) $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{X}_2]^-$. The uninegative anion is labile and dissociates to give paramagnetic (17e) $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{X}(\text{solvent})]$ in solution. This species has been reported¹⁶ to be important in subsequent substitution to give alkoxides and amido species, both detected electrochemically. Therefore, it may be suggested that during the reaction of $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{NH}_2)]$ with the alcohols ROH ($\text{R} = \text{Me}, \text{Et}, \text{Pr}^n, \text{Bu}^n$) in the presence of triethylamine, the HCl produced leads to the cleavage of the M–O and M–N bonds in the transient compounds, $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})(\text{NH}_2)(\text{OR})]$.

It has been reported¹⁵ that treatment of $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{X}(\text{Y})]$ ($\text{X} = \text{I}$ and $\text{Cl}, \text{Y} = \text{OR}; \text{X} = \text{OR}, \text{Y} = \text{OR}'$) with HCl causes cleavage of the M–O and M–N bonds and formation of $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{X}_2]$ ($\text{X} = \text{I}$ and Cl). This behaviour has also been observed^{12,14} for the compounds $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{HO})\text{X}(\text{NH}_2)]$ ($\text{X} = \text{Cr}, \text{Br}$ or I), and products of these reactions were identified by IR and ^1H NMR spectroscopy. Micro-analysis data obtained for the new complexes also

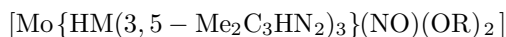
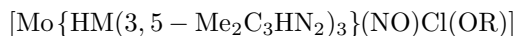
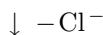
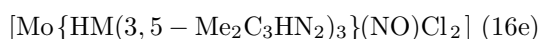
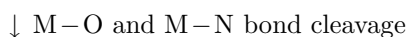
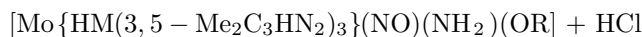
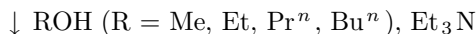
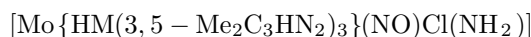
supported the proposed structures. Therefore, it may be thought that during the reaction of $[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})(\text{NH}_2)]$ with ammonia, the dihalogen compound $[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}_2]$ was formed as a transient species, which then reacted with the appropriate alcohol to yield the bisalkoxo-compound, $[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})(\text{OR})_2]$.

It has also been discovered¹² that prolonged reflux of $[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Br}_2]$ in ethanol afforded the bisalkoxo-compound $[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})(\text{OEt})_2]$ which now accounts for the formation of a bisalkoxo-type compound in the reactions of $[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{NH}_2)]$ with ROH (R = Me, Et, Prⁿ, Buⁿ). Therefore, a mechanism for the reaction of $[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{NH}_2)]$ with the alcohols ROH (R = Me, Et, Prⁿ, Buⁿ) could be suggested (Scheme 1).

Table 1. Analytical and Physical Data for the Bisalkoxo Complexes

Compound	m.p(°C)	M.W.	Analytical Data(%)*		
			C	H	N
$[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})(\text{Cl})(\text{NH}_2)]$	154	474.59	37.7(37.9)	5.85(5.90)	27.3(23.6)
$[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})(\text{OMe})_2]$	122	501.16	40.9(40.7)	6.08(6.03)	22.0(22.3)
$[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})(\text{OEt})_2]$	141	530.32	43.2(43.0)	5.53(6.65)	21.0(21.1)
$[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})(\text{OPr}^n)_2]$	128	558.37	42.8(43.0)	6.60(6.67)	19.8(20.0)
$[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})(\text{OBu}^n)_2]$	117	586.37	44.8(4.50)	6.90(7.04)	18.9(19.1)

*Calculate values are given in parantheses



Scheme 1. The mechanism suggested for the reaction of $[\text{Mo}\{\text{HM}(3, 5 - \text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{NH}_2)]$ with the alcohols ROH (R = Me, Et, Prⁿ, Buⁿ)

Spectroscopic Studies

The IR spectra of both the amido complex and the bisalkoxides (Table 2) exhibit the expected absorptions due to the $\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}$ ligand (*ca.* 2500 cm^{-1} due to $\nu(\text{HB})$ and 1400 cm^{-1} associated with the pyrazolyl ring). The NO stretching of the amido complex, $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{NH}_2)]$, gives an absorption band at 1670 cm^{-1} , and $\nu(\text{NH})$ reveals itself at 3309 cm^{-1} . For the complex $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{I}(\text{NH}_2)]$, $\nu(\text{NO})$ and $\nu(\text{NH})$ frequencies were reported¹⁴ as 1672 and 3252 cm^{-1} , respectively.

The IR spectra of the bisalkoxo complexes $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})(\text{OR})_2]$ ($\text{R} = \text{Me}, \text{Et}, \text{Pr}^n, \text{Bu}^n$) are very similar to those obtained¹⁵ by the reaction of the complex, $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{I}(\text{OR})]$ ($\text{R} = \text{Me}, \text{Et}, \text{Pr}^i, \text{CH}_2\text{Pr}^i$) with either silver acetate or triethylamine in a mixture of the appropriate alcohol and methylcyclohexane, as reported earlier. The $\nu(\text{NO})$ peak appears at $\sim 1637\text{ cm}^{-1}$ and no signal due to $\nu(\text{NH})$ was observed in any of the bisalkoxides, offering further proof that the complexes had no amido group.

The ^1H NMR spectrum of the complex, $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{NH}_2)]$ revealed signal at $\delta 2.30\text{-}2.60$ due to methyl protons. For protons attached to C(4) of the pyrazolyl protons, although three singlets were expected because of the asymmetry of these six-co-ordinate compounds, only two resonance of relative intensity 1:2 at $\delta 5.80\text{-}5.85$ were observed. This effect was previously observed by McCleverty et al.¹⁷ and was attributed to accidental degeneracy of two of the three H(4) resonances.

The signal due to the NH proton of the amido-group revealed itself as a broad singlet in the ^1H NMR spectrum of the $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{NH}_2)]$ at $\delta 11.30$ ppm. This signal was reported¹⁴ to appear in the range $\delta 11.96\text{-}12.80$ for the compounds $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{I}(\text{NHR})]$ ($\text{R} = \text{alkyl}$). The compound $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{I}(\text{NH}_2)]$ has been reported not to exhibit this signal¹⁴.

The ^1H NMR spectra of the bisalkoxo-complexes exhibit a group of signals around $\delta = 2.40$ ppm due to the methyl groups of the $\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}$ ligand. Resonances due to the proton attached to C-4 of the pyrazolyl groups occur near $\delta = 5.7$ ppm and these signals appear as two singlets (intensity 1:2).

The protons attached to the $\alpha\text{-C}$ atoms of the OR groups ($\text{R} = \text{Me}, \text{Et}, \text{Pr}^n, \text{Bu}^n$) in the complexes described here resonate at fields significantly lower than in the free alcohols. This effect has been observed before^{12,14} and is due to the strongly electron-withdrawing effect of the $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})]$ group. On the other hand, it has been reported¹⁵ that the $\beta\text{-protons}$ in the bis-alkoxides resonate at frequencies slightly higher than the field of their monoalkoxide analogues, which reflected a slight reduction in the electronegativity of the metal in the bis-substituted species relative to $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{OR}]$ ($\text{R} = \text{Me}, \text{Et}, \text{Pr}^n, \text{Bu}^n$).

Conclusion

This study was carried out in order to prepare monoalkoxo complexes of [tris(3,5-dimethylpyrazolyl)borate]molybdenum nitrosyl. Interestingly, bisalkoxo type complexes were obtained by the reaction of the amido complex, $[\text{Me}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{NH}_2)]$ with the alcohols ROH ($\text{R} = \text{Me}, \text{Et}, \text{Pr}^n, \text{Bu}^n$) in the presence of triethylamine. A mechanism involving the cleavage of the M–O and M–N bonds in $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})(\text{NH}_2)(\text{OR})]$, which was thought to be formed at first step, was suggested. It was found that IR and ^1H NMR spectroscopy data for the bisalkoxo complexes of [tris(3,5-dimethylpyrazolyl)borate]molybdenum nitrosyl.

Table 2. Infrared and ^1H NMR Data for the Complexes $[\text{Mo}\{\text{HM}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NOX}(\text{Y}))]$

Complex		IR(cm^{-1})			^1H NMR	
X	Y	$\nu(\text{NO})/ha$	$\nu(\text{NH})$	δ^b/ppm	A ^c	Assignment
Cl	NH ₂	1 679	3 309	11,30	2	s, br, NH ₂
				5,85	2	s, Me ₂ C ₃ H _N <u>N</u> ₂
				5,81	1	s, Me ₂ C ₃ H _N <u>N</u> ₂
				2,62	3	s, <u>Me</u> ₂ C ₃ H _N <u>N</u> ₂
				2,50	3	s, <u>Me</u> ₂ C ₃ H _N <u>N</u> ₂
				2,38	3	s, <u>Me</u> ₂ C ₃ H _N <u>N</u> ₂
				2,36	3	s, <u>Me</u> ₂ C ₃ H _N <u>N</u> ₂
				2,35	6	s, <u>Me</u> ₂ C ₃ H _N <u>N</u> ₂
OMe	OMe	1 637	—	5,80	2	s, <u>Me</u> ₂ C ₃ H _N <u>N</u> ₂
				5,64	1	s, <u>Me</u> ₂ C ₃ H _N <u>N</u> ₂
				5,10	6	s, OMe
				2,50	6	s, <u>Me</u> ₂ C ₃ H _N <u>N</u> ₂
				2,29	6	s, <u>Me</u> ₂ C ₃ H _N <u>N</u> ₂
				2,28	3	s, <u>Me</u> ₂ C ₃ H _N <u>N</u> ₂
				2,21	3	s, <u>Me</u> ₂ C ₃ H _N <u>N</u> ₂
OEt	OEt	1 637	—	5,80	2	s, Me ₂ C ₃ H _N <u>N</u> ₂
				5,70	1	s, Me ₂ C ₃ H _N <u>N</u> ₂
				5,54	4	m, AB Pair, CH ₂ CH ₃ , ³ J(HH) 7.0 Hz
				2,50	9	s, <u>Me</u> ₂ C ₃ H _N <u>N</u> ₂
				2,30	9	s, <u>Me</u> ₂ C ₃ H _N <u>N</u> ₂
				1,54	6	t, CH ₂ CH ₂ <u>CH</u> ₃ , ³ J(HH) 7.0 Hz
OPr ⁿ	OPr ⁿ	1 637	—	5,73	2	s, Me ₂ C ₃ H _N <u>N</u> ₂
				5,65	1	s, Me ₂ C ₃ H _N <u>N</u> ₂
				5,10	4	m, AB Pair, CH ₂ CH ₂ CH ₃
				2,48	9	s, <u>Me</u> ₂ C ₃ H _N <u>N</u> ₂
				2,24	9	s, <u>Me</u> ₂ C ₃ H _N <u>N</u> ₂
				1,70	4	m, CH ₂ CH ₂ <u>CH</u> ₃
				0,91	6	t, CH ₂ CH ₂ <u>CH</u> ₃ , ³ J(HH) 6.9 Hz
OBu ⁿ	OBu ⁿ	1 637	—	5,73	2	s, <u>Me</u> ₂ C ₃ H _N <u>N</u> ₂
				5,65	1	s, <u>Me</u> ₂ C ₃ H _N <u>N</u> ₂
				5,23	4	m, CH ₂ CH ₂ CH ₂ CH ₃ , AB Pair, ³ J(HH) 7.0 Hz
				2,69	9	s, Me ₂ C ₃ H _N <u>N</u> ₂
				4,28	9	s, Me ₂ C ₃ H _N <u>N</u> ₂
				1,71	4	m, (poorly resolved)
				1,36	4	m, CH ₂ CH ₂ CH ₂ <u>CH</u> ₃ , ³ J(HH) 7.0 Hz
				9,90	6	t, CH ₂ CH ₂ CH ₂ <u>CH</u> ₃ , ³ J(HH) 6.7 Hz

^aIn CH₂Cl₂, ^bIn CDCl₃, ^cRelative area

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