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# SYNTHESIS AND CHARACTERIZATION OF AMIDO and AMIDO(MONOALKYLAMIDO)NITROSYL-[TRIS(3,5-DIMETHYLPYRAZOLYL)BORATO]MOLYBDENUM COMPLEXES

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ABSTRACT

The chloro-amido complex [Mo{HB(3,5-$Me_2C_3HN_2)_3$}(NO)Cl($NH_2$)] was prepared by treating [Mo{HB(3,5-$Me_2C_3HN_2)_3$}(NO)$Cl_2$] with an excess of ammonia. The monoalkylamido complexes [Mo{HB(3,5-$Me_2C_3HN_2)_3$}-(NO)($NH_2$)(NHR)] (R = Me, Et, Pr-n and Bu-n) were obtained by the reaction of [Mo{HB(3,5-$Me_2C_3HN_2)_3$}(NO)Cl($NH_2$)] with the appropriate primary amines. The IR and $^1H$ NMR spectra of the new complexes were investigated.

## INTRODUCTION

The chloro-amido complex $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)Cl(NH_2)]$ was prepared by treating $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)Cl_2]$[1] with an excess of ammonia at room temperature. The previously reported iodo-amido complex, $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I(NH_2)]$, was synthesised by McCleverty et al.[2] by the reaction[3-5] of $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I_2]$ with ammonia.

McCleverty et al.[2,6-9] reported that the formally 16-electron complexes $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)X_2]$ (X = Cl or I) underwent substitution reactions with primary amines to give amide derivatives of the type $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)X(NHR)]$ (R = alkyl or aryl). It was suggested[10] that these reactions proceeded according to eq (1) in which a second molecule of amine was present to consume the liberated HX.

$$[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)X_2] + RNH_2 \longrightarrow [Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)X(NHR)] + RNH_3^+ + X^- \quad (1)$$

Magnetic resonance studies have shown[11,12] that paramagnetic intermediates were present during such reactions. The finding that $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I_2]$ could be readily reduced and that the resulting anion could readily dissociate iodide[11,12] provide an explanation of this phenomenon. McCleverty et al.[2] carried out the X-ray structure of the compound $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I(NHEt)]$ and reported that the molecule was six-coordinate with a linear Mo—N—O group and short Mo—NHEt bond.

The complexes $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)X(Y)]$ [X = F, Y = OEt, NHMe or SBu-n; X = Cl, Y = NHR (R = Me, Et, Bu-n, Ph, p-$MeC_6H_4$), $NMe_2$ and SR (R = Bu-n, $C_6H_{11}$, $CH_2Ph$, Ph); X = Br, Y = NHMe, $NMe_2$ and SBu-n] have been reported[13] and characterized spectroscopically. The properties of these complexes were generally similar to those of their iodo analogues[13].

The amido-alkoxo complexes [Mo{HB(3,5-$Me_2C_3HN_2)_3$}(NO)(OR)(NHR')] (R = Me, R' = H, Me, Et; R = Et, R' = H, Me, Et, Pr-n, $CH_2Ph$, $C_6H_{11}$) were prepared by treatment of [Mo{HB(3,5-$Me_2C_3HN_2)_3$}-(NO)I(OR)] with AgOCOMe in the presence of R'OH or $R'NH_2$.

The amine complexes [Mo{HB(3,5-$Me_2C_3HN_2)_3$}(NO)I($NHC_nH_{2n}$)] ($NHC_nH_{2n}$ = pyrrolidine, n = 4 or 5) and the amide complexes, [Mo{HB(3,5-$Me_2C_3HN_2)_3$}(NO)I($NC_nH_{2n}$)], ($NC_nH_{2n}$ = piperidine), were prepared by McCleverty et al.[10] by the reaction of the coordinatively unsaturated complex [Mo{HB(3,5-$Me_2C_3HN_2)_3$}(NO)$I_2$] with pyrrolidine and piperidine, respectively.

McCleverty et al.[8] have described and spectroscopically characterised the complexes [Mo{HB(3,5-$Me_2C_3HN_2)_3$}(NO)X(NHR)] (X = I, R = o-$C_6H_4Me$, 2,5-$Me_2C_6H_3$, $CHPh_2$, p-$C_6H_4CN$, p-$C_6H_4N_2Ph$, p-$C_6H_4N_2C_6H_4NO_2$-p, X = Cl, R = p-$C_6H_4I$). It was reported[8] that all of these compounds underwent at least an one-electron reduction process, some of which were reversible.

The arylamido complexes [Mo{HB(3,5-$Me_2C_3HN_2)_3$}(NO)I(NHR)] (R = Ph, $C_{10}H_7$ (2-naphthyl), $C_6H_4X$-p where X = Me, Et, OMe, OEt, F, Cl, Br, $CO_2Me$ or $NO_2$) were synthesised and the X-ray crystal structures of [Mo{HB(3,5-$Me_2C_3HN_2)_3$}(NO)I($NHC_6H_4$R-P)] (R = Me and OMe) were determined by McCleverty et al.[7] They have also prepared[14] the complexes [Mo{HB(3,5-$Me_2C_3HN_2)_3$}(NO)Cl($NHC_6H_4$Z-3)] (Z = F, Cl, Br, Me, OMe, COMe, $CF_3$, $NO_2$) and carried out spectroscopic investigations.

In this paper, the preparation of stable monomeric monoalkylamido complexes of the type [Mo{HB(3,5-$Me_2C_3HN_2)_3$}(NO)($NH_2$)(NHR)] (R = Me, Et, Pr-n, Bu-n) are described. The spectroscopic (IR and $^1$H NMR) characterisation of the new compounds are reported.

## RESULTS AND DISCUSSION

### Synthetic Studies

Reaction of the compound [Mo{HB(3,5-$Me_2C_3HN_2)_3$}(NO)$Cl_2$] with an excess of ammonia in toluene at room temperature afforded the orange

complex $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)Cl(NH_2)]$ (Fig.1). The orange compounds $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)X(NH_2)]$ (X = Br or I) were previously obtained[2] by treating the appropriate dihalogen complex, $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)X_2]$, with an excess of ammonia.

The compounds $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)(NH_2)(NHR)]$ (R = Me, Et, Pr-n, Bu-n) (Fig. 2) were prepared by refluxing $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)Cl(NH_2)]$ with an excess of the appropriate primary amines, $RNH_2$, in the presence of triethylamine in toluene. These monomeric monoalkylamido complexes were isolated as stable yellow solids.

McCleverty et al.[2,7,8] reported that the general preparation method of the monoalkyl(aryl) amido species $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I(NHR)]$ (R = alkyl or aryl) involved the addition of a two-fold excess of the appropriate amine to $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I_2]$ in dichloromethane at room temperature. It was suggested[2,7,8] that excess of amine was consumed as it facilitated the removal of HI formed during the reaction of eq (2).

$$[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I_2] + 2NH_2R \longrightarrow [Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I(NHR)] + [NH_3R]I \qquad (2)$$

It was reported[8] that the conditions required to form $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I(NHR)]$ were milder than those used to produce $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)Cl(NHR)]$. The latter needed refluxing conditions either in dichloromethane or toluene. For the synthesis of the compounds $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)(NH_2)(NHR)]$ (R = Me, Et, Pr-n, Bu-n) the starting complex, $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)Cl(NH_2)]$, was refluxed with the appropriate amine in the presence of triethylamine in toluene, proving that the chloride analogues were less reactive compared to the iodo species.

During the reactions of $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)Cl(NH_2)]$ with primary amines, $RNH_2$ (R = Me, Et, Pr-n, Bu-n), it was found that HCl produced with the chloride abstracting reagent triethylamine could lead to

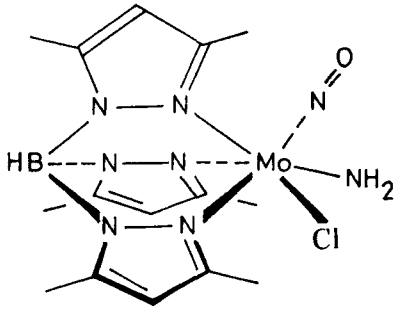
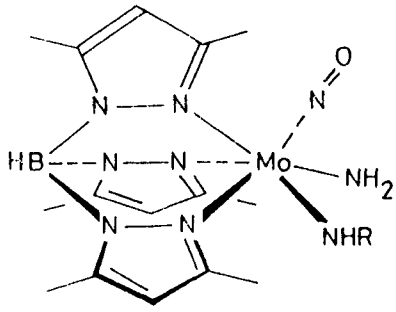



Figure 1. The Structural Formulae of the Compound [Mo{HB(3,5-$Me_2$-$C_3HN_2)_3$(NO)Cl($NH_2$)].




R = Me, Et, Pr-n, Bu-n)

Figure 2. The Structural Formulae of the Complexes [Mo{HB(3,5-$Me_2$-$C_3HN_2)_3$}(NO)($NH_2$)(NHR)] (R = Me, Et, Pr-n, Bu-n)

Mo—N bond cleavage on prolonged refluxing. Indeed, when the reaction mixtures, were left refluxing overnight, a dramatic decrease in yields was observed. This is not a surprising observation as it was known[4] that treatment of [Mo{HB(3,5-$Me_2C_3HN_2)_3$}(NO)X(Y)] (X = I, Y = OR; X = OR, Y = OR', X = OR, Y = NHR'; where R and R' are both alkyl) with HCl caused cleavage of the M—O and M—N bonds and formation of [Mo{HB(3,5-$Me_2C_3HN_2)_3$}(NO)X(Y)] (X = I, Y = Cl; X = Y = Cl).

Spectral Studies

The IR spectra of both the amido complex $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)Cl(NH_2)]$ and amido(monoalkylamido) complexes $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)(NHR)]$ (R = Me, Et, Pr-n, Bu-n) exhibit the expected absorptions due to the $\{HB(3,5\text{-}Me_2C_3HN_2)_3\}$ ligand (*ca.* 2500 $cm^{-1}$ due to $\upsilon$(BH) and 1400 $cm^{-1}$ associated with the pyrazolyl ring). These values are similar to the ones previously suggested by McCleverty et al.[2-7] The NO stretching frequency of the amido complex $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)Cl(NH_2)]$ occurs at 1670 $cm^{-1}$ and $\upsilon$(NH) reveals itself at 3309 $cm^{-1}$. These observations are in accord with the characteristic group frequencies given by Silverstein et al.[15]. For the complex $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3(NO)I(NH_2)]$ the $\upsilon$(NO) and $\upsilon$(NH) frequencies were reported[2] at 1672 and 3252 $cm^{-1}$ respectively.

The IR spectra of the complexes $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)\text{-}(NH_2)(NHR)]$ (R = Me, Et, Pr-n, Bu-n) exhibit the expected absorptions due to the $[HB(3,5\text{-}Me_2C_3HN_2)_3]$ ligand (*ca.* 2500 $cm^{-1}$ due to $\upsilon$(BH) and 1400 $cm^{-1}$ associated with the pyrazolyl ring). The NO stretching frequency of the amido(monoalkyl)amido complexes reveals itself in the range between 3225-3265 $cm^{-1}$ and the $\upsilon$(NH) frequencies fall in the range 1639-1653 $cm^{-1}$ (Table I). The former frequency was reported[2] to appear in the range 1640-1672 $cm^{-1}$ for the previously reported iodo complexes, $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I(NHR)]$ (R = H, Me, Et, Pr-n, Pr-i, Bu-n, Bu-t, $C_6H_{11}$, $C_3H_5$ or $CH_2Ph$). As it was pointed out above, the $\upsilon$(NO) stretching frequency was found as 1679 $cm^{-1}$ for the complex $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)Cl(NH_2)]$. The $\upsilon$(NO) value for $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I(NH_2)]$ was reported[2] to appear at 1672 $cm^{-1}$. These higher values, compared to the monoalkylamido species, $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)X(NHR)]$ (X = I[2] and $NH_2$), are understandable as the basicity of NHR (R = alkyl) is greater than that of $NH_2$. McCleverty et al.[2] suggested that, in general, $\upsilon$(NO) absorptions do not appear to be influenced by the electronic nature of the alkyl group. For the arylamido compounds, $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I(NHR)]$ (R =

Ph, $C_{10}H_7$ (2-napthyl), $C_6H_4X$-p where X = Me, Et, OMe, OEt, F, Cl, Br, I, $CO_2Me$, $NO_2$ or CN), the $\upsilon$(NO) absorptions were reported[8] to appear in the range 1666-1676 cm$^{-1}$.

The $^1$H NMR spectrum of the complex [Mo{HB(3,5-$Me_2C_3HN_2)_3$}-(NO)Cl($NH_2$)] revealed signals at $\delta$ 2.30-2.60 (Table I) due to the methyl protons. For the protons attached to C(4) of the pyrazol ring, although the singlets were expected because of the asymmetry of these six-coordinate compounds, only two resonances of the relative intensity 1:2 at $\delta$ 5.80-5.85 were observed. This effect has been observed by McCleverty et al.[11,12] before 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 $^1$H NMR spectrum of [Mo{HB-(3,5-$Me_2C_3HN_2)_3$}(NO)Cl($NH_2$)] at $\delta$ 11.30 ppm. This signal was reported[8] to appear in the range $\delta$ 10.0-13.5 for the compounds [Mo{HB-(3,5-$Me_2C_3HN_2)_3$}(NO)I(NHR)] (R = o-$C_6H_4$Me, 2,5-$Me_2C_6H_3$, $CHPh_2$, p-$C_6H_4CN$, p-$C_6H_4N_2$Ph, p-$C_6H_4N_2C_6H_4NO_2$-p) and the compound [Mo{HB(3,5-$Me_2C_3HN_2)_3$}(NO)I($NH_2$)] did not exhibit this signal.

The $^1$H NMR spectra of the complexes [Mo{HB(3,5-$Me_2C_3HN_2)_3$}-(NO)($NH_2$)(NHR)] (R = Me, Et, Pr-n, Bu-n) showed six signals in the range 2.21-2.59 ppm due to the methyl protons and in the range 5.76-5.87 ppm for the protons attached to C(4) of the pyrazolyl ring. This indicates that the complexes have the expected six-coordinate structure and there is no plane of symmetry in the species. These data were similar to the previously values reported by McCleverty et al.[2,8,13] for [Mo{HB(3,5-$Me_2C_3HN_2)_3$}-(NO)X(NHR)] (X = I, R = alkyl or aryl; X = Cl, R = alkyl). All the complexes were expected to exhibit three resonances due to the protons attached to C(4) of the three non-equivalent pyrazolyl rings as they are asymmetric. The complexes [Mo{HB(3,5-$Me_2C_3HN_2)_3$}(NO)($NH_2$)(NHR)] (R = Me and Et) showed these expected three signals whereas in case of R = Pr-n and Bu-n, only two resonances at the relative intensities 1:2 were observed. This effect has been observed by McCleverty et al.[2,3,8,13] before and has been attributed to accidental degeneracy of two of the three H(4) resonances.

Table I. Infrared and $^1H$ NMR Data For the Complexes $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)(X)(Y)]$

| Complex | | IR ($cm^{-1}$)[a] | | $^1H$ NMR | | |
|---|---|---|---|---|---|---|
| X | Y | υ(NO) | υ(NH) | δ[b]/ppm | A[c] | Assignment |
| Cl | $NH_2$ | 1679 | 3309 | 11.30 | 2 | s, br, $NH_2$ |
| | | | | 5.85 | 2 | s, $Me_2C_3\underline{H}N_2$ |
| | | | | 5.81 | 1 | s, $Me_2C_3\underline{H}N_2$ |
| | | | | 2.62 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 2.50 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 2.38 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 2.36 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 2.35 | 6 | s, $\underline{Me}_2C_3HN_2$ |
| $NH_2$ | NHR (R = Me) | 1639 | 3265 | 12.69 | 1 | s, br, $NH_2$ |
| | | | | 11.72 | 2 | s, br, N$\underline{H}$Me |
| | | | | 5.82 | 1 | s, $Me_2C_3\underline{H}N_2$ |
| | | | | 5.79 | 1 | s, $Me_2C_3\underline{H}N_2$ |
| | | | | 5.76 | 1 | s, $Me_2C_3\underline{H}N_2$ |
| | | | | 4.16 | 3 | d, NH$\underline{Me}$ |
| | | | | 2.57 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 2.51 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 2.43 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 2.39 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 2.31 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 2.30 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| $NH_2$ | NHR (R = Et) | 1651 | 3248 | 12.54 | 1 | m, N$\underline{H}$Et |
| | | | | 11.64 | 2 | s, br, $NH_2$ |
| | | | | 5.87 | 1 | s, $Me_2C_3\underline{H}N_2$ |
| | | | | 5.84 | 1 | s, $Me_2C_3\underline{H}N_2$ |
| | | | | 5.77 | 1 | s, $Me_2C_3\underline{H}N_2$ |
| | | | | 4.49 | 2 | m, NHC$\underline{H}_2$Me |
| | | | | 2.53 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 2.50 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 2.42 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 2.38 | 3 | s, $\underline{Me}_2C_3HN_2$ |

Table I continued

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | | 2.35 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 2.31 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 1.42 | 3 | t, $^3J$ 7.0Hz, $NCH_2\underline{CH}_3$ |
| $NH_2$ | NHR (R = Pr-n) | 1653 | 3274 | 12.51 | 1 | br, N<u>H</u>Pr-n |
| | | | | 11.60 | 2 | s, br, $NH_2$ |
| | | | | 5.83 | 2 | s, $Me_2C_3\underline{H}N_2$ |
| | | | | 5.78 | 1 | s, $Me_2C_3\underline{H}N_2$ |
| | | | | 4.45 | 2 | m, $NHCH_2Et$ |
| | | | | 2.52 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 2.51 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 2.46 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 2.41 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 2.37 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 2.22 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 1.79 | 2 | m, $NHCH_2C\underline{H}_2Me$ |
| | | | | 1.08 | 3 | t, 3J 7.1Hz, NH $(CH_2)_2C\underline{H}_3$ |
| $NH_2$ | NHR (R = Bu-n) | 1641 | 3225 | 12.70 | 1 | br, N<u>H</u>Bu-n |
| | | | | 11.61 | 2 | s, br, $NH_2$ |
| | | | | 5.81 | 2 | s, $Me_2C_3\underline{H}N_2$ |
| | | | | 5.79 | 1 | s, $Me_2C_3\underline{H}N_2$ |
| | | | | 4.48 | 2 | m, $NHC\underline{H}_2Pr$-n |
| | | | | 2.59 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 2.52 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 2.40 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 2.35 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 2.33 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 2.21 | 3 | s, $\underline{Me}_2C_3HN_2$ |
| | | | | 1.86 | 2 | m, $NHCH_2C\underline{H}_2Et$ |
| | | | | 1.63 | 2 | m, NH $(CH_2)_2C\underline{H}_2Me$ |
| | | | | 0.99 | 3 | t, $^3J$ 6.8 Hz, $NH(CH_2)_2C\underline{H}_3$ |

[a]In $CH_2Cl_2$, [b]In $CDCl_3$, [c]Relative area

All the complexes exhibit broad singlets in the range 11.60-12.69 ppm due to the NH proton of the $NH_2$ group. The δ(NH) values for the NHR (R = Me, Et, Pr-n, Bu-n) ligands appear in the range 11.72-12.70 ppm which is in accord with the previously reported[2,8,13] values for the compounds [Mo{HB(3,5-$Me_2C_3HN_2)_3$}(NO)I(NHR)] (R = Me, Et, Pr-n, Bu-n).

The chemical shifts of the protons attached to the α-C atoms of the alkyl groups in [Mo{HB(3,5-$Me_2C_3HN_2)_3$}(NO)($NH_2$)(NHR)] (R = Me, Et, Pr-n, Bu-n) resonate at fields significantly lower than their δ values in the free ligand (δ 4.16-4.49). This observation has been made before by McCleverty et al.[3,4,6] and has been attributed to the strongly electronegative [Mo{HB(3,5-$Me_2C_3HN_2)_3$}(NO)X] (X = I or Cl) group which caused a net withdrawal of electron density from the amido group.

## EXPERIMENTAL

All the reagents were used as supplied without further purification. Triethylamine was dried over sodium. Solvents were redistilled prior to use from drying agents according to standard methods. All yields are based on the starting metal-containing compound.

IR spectra were measured using a PE 1600 FTIR spectrophotometer. $^1H$ NMR spectra were recorded on a JEOL GX270 instrument. Elementel analyses were determined by the Microanalytical Laboratory of the School of Chemistry, University of Bristol.

### Preparation of [Mo{HB(3,5-$Me_2C_3HN_2)_3$}(NO)Cl($NH_2$)]

A solution of the compound [Mo{HB(3,5-$Me_2C_3HN_2)_3$}(NO)$Cl_2$] (0.20 g, 0.40 mmol) and an excess of ammonia solution (0.1 mL, 6.0 mmol) in toluene (20 mL) at 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 (1:4) affording the desired product as orange microcrystals of [Mo{HB

$(3,5\text{-}Me_2C_3HN_2)_3\}$-$(NO)Cl(NH_2)]$, m.p 154 °C (decomp); yield 0.16 g (86 %). *Anal.* Found: C, 37.7, H, 5.85, N, 23.7 %. Calcd. for $C_{15}H_{24}N_8OBClMo$ (474.59): C, 37.9, H, 5.90, N, 23.6 %.

Preparation of $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)(NH_2)(NHMe)]$

A solution of $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)Cl(NH_2)]$ (0.2 g, 0.42 mmol) and excess methylamine (0.2 mL, 5.0 mmol) in toluene (20 mL) was refluxed for *ca.* four hours during which time the colour changed to orange-yellow. The solvent was removed *in vacuo*. Diisopropylether was added and methylamine iodide was filtered off. Slow evaporation followed by an addition of hexane afforded yellow microcrystals of $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)(NH_2)(NHMe)]$, m.p 131°C (decomp); yield, 0.15 g (77 %). *Anal.* Found: C, 40.7, H, 6.12, N, 26.6 %. Calcd. for $C_{16}H_{28}N_9OBMo$ (469.21): C, 40.9, H, 6.01, N, 26.8 %.

Preparation of $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)(NH_2)(NHEt)]$

This complex was prepared by treating $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}$-$(NO)Cl(NH_2)]$ (0.2 g, 0.42 mmol) with an excess of ethylamine (0.26 mL, 5.0 mmol) in a manner similar to that described for the preceding complex. Recrystallisation from dichloromethane-hexane (1:4) afforded microcrystals of $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)(NH_2)(NHEt)]$, m.p 128°C (decomp); yield, 0.15 g (74 %). *Anal.* Found: C, 42.0, H, 6.16, N, 26.3 %. Calcd. for $C_{17}H_{30}N_9OBMo$ (483.23): C, 42.2, H, 6.25, N, 26.0 %.

Preparation of $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)(NH_2)(NHPr\text{-}n)]$

The preparation of this complex was similar to that of $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)(NH_2)(NHMe)]$ except that n-propylamine (0.41 mL, 5.0 mmol) was used. The desired product $[Mo\{HB(3,5\text{-}Me_2$-$C_3HN_2)_3\}(NO)(NH_2)(NHPr\text{-}n)]$ was isolated as yellow microcrystals, m.p 121°C (decomp); yield, 0.14 g (69 %). *Anal.* Found: C, 43.2, H, 6.29, N, 25.5 %. Calcd. for $C_{18}H_{32}N_9OBMo$ (497.26): C, 43.4, H, 6.48, N, 25.3 %.

The preparation of [Mo{HB(3,5-$Me_2C_3HN_2)_3$}(NO)($NH_2$)(NHBu-n)]

The preparation of this complex was similar to that of [Mo{HB(3,5-$Me_2C_3HN_2)_3$}(NO)($NH_2$)(NHMe)] except that n-butylamine (0.49 mL 5.0 mmol) was used. The desired product [Mo{HB-(3,5-$Me_2C_3HN_2)_3$}(NO)($NH_2$)(NHBu-n)] was isolated as yellow microcrystals, m.p 117°C (decomp); yield, 0.12 g (60 %). *Anal.* Found: C, 44.3 H, 6.55, N, 24.8 %. Calcd. for $C_{19}H_{34}N_9OBMo$ (511.29): C, 44.6, H, 6.68, N, 24.6 %.

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