Reaction of Di-iodonitrosyl[tris(3,5-dimethylpyrazolyl)borato]-molybdenum with α,ω-Alkanediols, 2-Chloro-, and 2-Methoxy-ethanol †

By **Gianfranco Denti, Jon A. McCleverty,*** and **Andrzej Włodarczyk,** Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham B15 2TT

The complexes $[Mo\{HB(3,5-Me_2C_3HN_2)_3\}(NO)I\{O(CH_2)_nR\}]$ [R = OH, n = 2—6; R = Cl or OMe, n = 2] and $[Mo\{HB(3,5-Me_2C_3HN_2)_3\}(NO)\{O(CH_2)_nOH\}_2]$ (n = 2) have been prepared by the reaction of $[Mo\{HB(3,5-Me_2C_3HN_2)_3\}(NO)I_2]$ with the appropriate α,ω-alkanediol, 2-chloro- or 2-methoxy-ethanol. No evidence could be found for chelated complexes of the type $[\overline{Mo\{HB(3,5-Me_2C_3HN_2)_3\}(NO)\{O(CH_2)_nO}\}]$.

In previous papers [2,3] we have described the formation of moisture-stable mono- and bis-alkoxide complexes of the type $[Mo\{HB(3,5-Me_2C_3HN_2)_3\}(NO)I(OR)]$. We now describe our attempts to prepare related complexes from α,ω-alkanediols. We undertook this work in order to establish whether diols would form chelate rings with the $Mo\{HB(3,5-Me_2C_3HN_2)_3\}(NO)$ group, or whether they would form simple mono- and/or bis-alkoxides with uncomplexed OH groups.

EXPERIMENTAL

The complex $[Mo\{HB(3,5-Me_2C_3HN_2)_3\}(NO)I_2]$ was prepared from $[Mo\{HB(3,5-Me_2C_3HN_2)_3\}(NO)(CO)_2]$ as previously described.[2] Hydrogen-1 n.m.r. and i.r. spectra were measured using Varian XL100 and Perkin-Elmer 457 and R34 spectrometers. Elemental analyses were obtained by the microanalytical laboratories of the Departments of Chemistry at the Universities of Sheffield and Birmingham. The yields are quoted relative to the starting molybdenum complex.

General Procedures for the Preparation of the Complexes $[Mo\{HB(3,5-Me_2C_3HN_2)_3\}(NO)I\{O(CH_2)_nOH\}]$.—$[Mo\{HB(3,5-Me_2C_3HN_2)_3\}(NO)I_2]$ (0.5 g) was dissolved in dry benzene (50 cm^3) and an excess of the appropriate α,ω-alkanediol was added. The mixture was refluxed overnight under N_2, and from the bright green solution a very pale red oil was isolated on cooling and this was discarded. When all the benzene had been evaporated *in vacuo*, a green powder remained. This compound was recrystallised from benzene–n-heptane mixtures, affording the monoalkoxide *complex* as green crystals (65—85% yields). Complexes derived from $HO(CH_2)_nOH$ (n = 2—6), and also $HOCH_2CH_2Cl$ and $HOCH_2CH_2OMe$, were made by this method. Prolonged heating of the compound in organic solvents caused decomposition.

General Procedure for the Preparation of the Complexes $[Mo\{HB(3,5-Me_2C_3HN_2)_3\}(NO)\{O(CH_2)_nOH\}_2]$.—The procedure outlined above was followed except that dry, freshly distilled tetrahydrofuran (thf) was used as solvent and $Na_2[CO_3]$ (2 : 1 ratio with respect to diol) was added as a 'deprotonating' agent. The yield of the pink *complexes* was generally 75% but only the complex derived from ethane-1,2-diol afforded satisfactory elemental analyses. Purification could not be effected by column chromatography on alumina or cellulose.

RESULTS AND DISCUSSION

Reaction of $[Mo\{HB(3,5-Me_2C_3HN_2)_3\}(NO)I_2]$ with an excess of the α,ω-alkanediols $HO(CH_2)_nOH$ (n = 2—6) afforded the *mono*-alkoxides $[Mo\{HB(3,5-Me_2C_3HN_2)_3\}(NO)I\{O(CH_2)_nOH\}]$. The species $[Mo\{HB(3,5-Me_2C_3HN_2)_3\}(NO)I\{O(CH_2)_2Q\}]$ (Q = Cl or OMe) were obtained similarly (analytical data, Table 1). These complexes are green, which is the characteristic colour for species of the general type $[Mo\{HB(3,5-Me_2C_3HN_2)_3\}(NO)I(OR)]$.[2]

During the preparation of the monoalkoxides, traces of pink species were observed. It is very likely that this colour was due to small amounts of the bisalkoxides and, indeed, pink $[Mo\{HB(3,5-Me_2C_3HN_2)_3\}(NO)\{O(CH_2)_nOH\}_2]$ was obtained in good yield when $Na_2[CO_3]$ was added to the reaction mixture. However, only the compound derived from ethylene glycol (n = 2) afforded satisfactory analytical and spectral data (Table 2); all other bisalkoxides could not be purified without decomposition.

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† Regarded as Part 14 in the series Nitrosyl Complexes of Molybdenum.[1]

TABLE 1

Analytical data (%) for $[Mo\{HB(3,5-Me_2C_3HN_2)_3\}(NO)IX]$ and $[Mo\{HB(3,5-Me_2C_3HN_2)_3\}(NO)X_2]$ [a]

X	C	H	I	N
$OCH_2CH_2OCH_3$	35.60 (34.60)	5.10 (4.70)	20.90 (20.30)	16.25 (15.70)
OCH_2CH_2Cl [b]	33.35 (32.40)	4.75 (4.15)	19.60 (20.15)	15.15 (15.55)
OCH_2CH_2OH	34.75 (33.40)	4.90 (4.45)	20.85 (20.75)	15.25 (16.05)
$OCH_2CH_2CH_2OH$	33.05 (34.60)	4.85 (4.70)	20.95 (20.30)	14.90 (15.70)
$OCH_2(CH_2)_2CH_2OH$	37.05 (35.70)	5.35 (4.90)	21.25 (19.85)	14.75 (15.35)
$OCH_2(CH_2)_3CH_2OH$	35.95 (36.80)	4.90 (5.10)	20.30 (19.45)	14.85 (15.00)
$OCH_2(CH_2)_4CH_2OH$	36.00 (37.80)	4.95 (5.30)	21.60 (19.00)	15.95 (14.70)
OCH_2CH_2OH [c]	40.95 (41.85)	5.75 (5.90)		17.35 (18.00)

[a] Calculated values in parentheses. [b] Analysis for Cl: 6.05 (5.65)%. [c] Only one bisalkoxide is characterised, where X = OCH_2CH_2OH.

TABLE 2

Spectroscopic data for $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)IX]$ and $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)X_2]$

	I.r.[a]		Hydrogen-1 n.m.r.[b]		
X	ν(NO)	ν(OH)[c]	CH_3[d]	CH_2[e]	$(Me_2CHN_2)_3$[d]
$OCH_2CH_2OCH_3$	1 668		1.89(2), 2.06, 2.25, 2.68, 2.70, 3.01	3.59,[f,g] 5.75[f,h]	5.23, 5.42, 5.57
OCH_2CH_2Cl	1 675		1.86(2), 2.04, 2.13, 2.59, 2.66	3.55,[g] 5.63[h]	5.22, 5.39, 5.56
OCH_2CH_2OH	1 673	3 410	1.85, 1.87, 2.03, 2.20, 2.61, 2.69	3.82,[f,g] 5.56[h]	5.24, 5.39, 5.55
$OCH_2CH_2CH_2OH$	1 670	3 425	1.88(2), 2.06, 2.23, 2.68, 2.72	1.32, 3.48,[g] 5.78[h]	5.29, 5.41, 5.57
$OCH_2(CH_2)_2CH_2OH$	1 666	3 415	1.88(2), 2.06, 2.24, 2.67, 2.73	1.35(2), 3.29,[g] 5.69[h]	5.28, 5.43, 5.61
$OCH_2(CH_2)_3CH_2OH$	1 672	3 400	1.88(2), 2.06, 2.25, 2.67, 2.73	1.30(3), 3.32,[g] 5.65[h]	5.28, 5.42, 5.60
$OCH_2(CH_2)_4CH_2OH$	1 668	3 395	1.87(2), 2.05, 2.25, 2.67, 2.73	1.25(4), 3.32,[g] 5.65[h]	5.28, 5.42, 5.60
OCH_2CH_2OH[i]		3 260 3 350	2.28(6), 2.29(3), 2.34(3), 2.52(6)	3.83(4),[f] 5.24, 5.54(4)[f]	5.74(1), 5.79(2)

[a] In cm^{-1}, KBr pellet. [b] δ (p.p.m.) relative to $SiMe_4 = 0$, C_6D_6 solution (relative area in parentheses). [c] Very broad. [d] Singlets. [e] Multiplets. [f] Approximate AB pairs. [g] Terminal methylene groups. [h] Mo-O-CH_2 methylene groups. [i] Only one bisalkoxide, $X = OCH_2CH_2OH$, was characterised fully.

In none of the reactions described did we obtain the chelated species $[\overline{Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)\{O(CH_2)_nO}\}]$, nor could we induce cyclisation of the $Mo{-}O(CH_2)_nOH$ group by treatment of the mono-iodo-alkoxide with Tl^+ or Ag^+.

The i.r. spectra of these new compounds were generally consistent with their formations. Thus in the mono- and bis-alkoxides, ν(NO) occurred in the range 1 666—1 675 cm^{-1} and at 1 642 cm^{-1}, respectively, which was expected from our earlier work.[2] The complexes obtained for the α,ω-alkanediols exhibited ν(OH) in the expected region. The ^1H n.m.r. spectra of these compounds also agreed with their formulations, and were generally similar to those obtained from the mono- and bis-alkoxides described previously.[2,3] Thus, the somewhat anomalous low-field shift of the protons attached to the C atom α to the metal-bound O atom was observed ($\delta = 5.2$—5.8 p.p.m.). This is due to the strongly electron withdrawing properties of the Mo atom which induces a substantial deshielding of the α-C and α-H atoms. In none of the spectra obtained from complexes derived from the alkanediols could the unbound O*H* proton be detected. In the monoalkoxide species, the 4-H protons of the pyrazole groups appeared as three singlets, whereas in $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)(OCH_2CH_2OH)_2]$ they appeared as two resonances of relative intensity 1 : 2. These observations are entirely consistent with the expected six-co-ordinate geometry of these compounds.[2,3]

These complexes are air and moisture stable, although cleavage of the Mo–O bonds can be effected by acid. They formally contain Mo^{III} (regarding NO is a neutral ligand) which contrasts with other known alkanediolato-complexes of molybdenum,[4] *e.g.* $[MoO_2(OC_2H_4OH)_2]$ and $[MoOF_4(OCH_2CH_2O)]^-$, which are derivatives of Mo^{VI}.

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