Reactions of [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}I_2] with some Cyclic Ethers to form Alkoxide Complexes

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The complex [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}I_2] reacts with oxacyclobutane, oxacyclopentane (tetrahydrofuran), or oxacycloheptane, in the presence of traces of moisture, to produce the diamagnetic alkoxide derivatives [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}I{O$(CH_2)_n$I}] (n = 3, 4, or 6 respectively). The reaction with methyloxacyclopropane (1,2-epoxypropane) affords a complex mixture of isomers, only one of which could be isolated in a pure form. The spectroscopic data were in accord with the formulation of this compound as [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}-I{OCH(Me)CH_2I}]. In the case of oxacyclohexane (tetrahydropyran) only the paramagnetic complex [Mo(NO){HB(3,5-$Me_2C_2N_2H)_3$}I(3,5-$Me_2C_3N_2H_2$)] could be isolated.

The diamagnetic complex [Mo(NO)LI_2] [L = tris(3,5-dimethylpyrazol-1-yl)hydroborate] is a formally 16-electron co-ordinatively unsaturated species which is reactive towards iodide substitution by a variety of reagents. Thus with alcohols, thiols, or alkylamines, for example, the derivatives [Mo(NO)-LI(XR)] (X = O, S, or NH; R = alkyl) are formed readily.[1] These are also diamagnetic, formally 16-electron, complexes but magnetic resonance studies have indicated that paramagnetic species are present during the reactions in which they are formed. The discovery[2] that [Mo(NO)LI_2] is redox active, undergoing a facile one-electron reduction reaction, led to the proposal that the 17-electron complexes [Mo(NO)$LI_2]^-$ and [Mo(NO)LI(L′)] [L′ = a neutral donor ligand such as the solvent, *e.g.*, tetrahydrofuran (thf) or acetonitrile] might be involved in the mechanism of formation of [Mo(NO)LI(XR)]. Attempts to isolate the 17-electron complex [Mo(NO)LI(thf)] were unsuccessful but the reduced diiodide was obtained[3] in the form of [Mo(NO)L(μ-I)$_2$Li(OEt$_2)_2$], which is air and moisture sensitive. Air-stable 17-electron complexes containing the $\{Mo(NO)L\}^{3+}$ moiety can be obtained[4] with heterocyclic ligands, *e.g.*, $[Mo(NO)L(A)_2]^+$ (A = pyridine, imidazole, *N*-methylimidazole, pyrazole, 3,5-dimethylpyrazole, or acetonitrile).[4–6] However, attempts to prepare the neutral monosubstituted derivatives [Mo(NO)LI(A)] were unsuccessful.[4,5] In the course of these studies it was found that a complex formulated as [Mo(NO)LI{O$(CH_2)_4$I}] could be isolated from the reaction between [Mo(NO)LI_2] and thf. Since reports of the formation of alkoxides from cyclic ethers are rare we have investigated the reactions between [Mo(NO)LI_2] and cyclic ethers having ring sizes from three to seven. An unexpected finding in this study was the formation, in one instance, of the 17-electron complex [Mo(NO)LI(3,5-$Me_2C_3N_2H_2$)] in which only one iodide ligand is substituted by the heterocyclic nitrogen ligand.

Results

Reaction of [Mo(NO)LI_2] *with Tetrahydrofuran.*—The compound [Mo(NO)LI_2] could be recovered unchanged from rigorously dried thf after 3 d at reflux under dinotrogen. However, if the solution was exposed to air, or if a drop of water was added, a green solution formed. Column chromatography of the reaction mixture on silica gel afforded one major green product, (**1**). The i.r. spectrum of (**1**) exhibited ν(BH) at 2 550 cm^{-1} along with other bands attributable to the presence of L. The colours of complexes containing the $\{Mo(NO)L\}^{2+}$ core are quite characteristic[1] and the dark green colour of (**1**) was typical of an iodoalkoxide. This view was supported by the observation of ν(NO) at 1 670 cm^{-1} compared to the typical value of 1 675 cm^{-1} for [Mo(NO)LI(OR)] (R = alkyl).[1] The 400 MHz ^1H n.m.r. spectrum of (**1**) in $CDCl_3$ was also consistent with such a formulation with the alkoxide being derived from thf. Three signals, each of relative area 1 and attributable to the pyrazolyl H^4 protons of L, were observed at δ 5.90, 5.86, and 5.84, while six signals, each of relative area 3 and attributable to the pyrazolyl methyl groups, were observed at δ 2.51, 2.44, 2.42, 2.38, 2.36, and 2.36. The methylene protons of the $-CH_2-$ group adjacent to the alkoxide oxygen appeared as an eight line multiplet of area 2 centred at δ 5.61. This low-field shift, and appearance as an AB pair coupled to the β-CH_2 of the alkoxide, is typical of complexes of the general formula [Mo(NO)LI(OCH_2CH_2R)] (R = H or CH_2Br).[1,7] In addition to these signals, a complex multiplet of relative area 4 centred at δ 2.03 and a 10-line multiplet of relative area 2 centred at δ 3.24 p.p.m. were observed. Comparison with the ^1H n.m.r. spectrum of the known complex [Mo(NO)LI(OCH_2CH_2-CH_2Br)] indicates that (**1**) may be formulated as [Mo(NO)-LI{O$(CH_2)_4$I}]. Thus the signal at δ 3.24 may be assigned to the terminal $-CH_2$I group and that at δ 2.03 p.p.m. to the β- and γ-methylene protons of the 4-iodobutoxide ligand. The presence of iodine as the 4 substituent of the butoxide was confirmed by iodine analysis.

Reactions of [Mo(NO)LI_2] *with Methyloxacyclopropane and Oxacyclobutane.*—The reactions of [Mo(NO)LI_2] with the smaller ring cyclic ethers $\overline{OCH_2CHMe}$ and $\overline{O(CH_2)_2CH_2}$ proceeded more rapidly than with thf. Thus the reaction with $\overline{O(CH_2)_2CH_2}$ appeared essentially complete after 10 min at room temperature. The reaction products were separated by chromatography, and the principal product, (**2**) was again found to be green. However, a pink fraction, (**3**), was also isolated from this reaction. The i.r. spectra of (**2**) and (**3**) exhibited ν(BH) along with other bands attributable to L. The green colour of (**2**) and the observation of ν(NO) at 1 670 cm^{-1} were consistent with the formulation of this reaction product as an alkoxide. The 400 MHz ^1H n.m.r. spectrum in $CDCl_3$ exhibited signals at δ 5.89, 5.85, and 5.83 of relative areas 1:1:1

attributable to the pyrazolyl H^4 protons and signals at δ 2.50, 2.42, 2.41, 2.37, 2.37, and 2.35 each of area 3 attributable to the pyrazolyl methyl protons. The α-methylene protons of the alkoxide ligand appeared as a nine-line multiplet of area 2 centred at δ 5.62. This feature of the spectrum was better resolved than in (**1**) owing to a larger separation of the A and B components of the ABX_2 system, so that shifts $\delta_A = 5.65$ and $\delta_B = 5.59$ could be assigned with $^2J_{AB} = 12$ Hz and $^3J_{AX} = {}^3J_{BX} = 6$ Hz. The β-methylene signals of the alkoxide ligand appeared as a multiplet beneath the pyrazolyl methyl protons at δ *ca.* 2.45. The signals attributable to the terminal $-CH_2I$ group appeared as a 10-line multiplet centred at δ 3.30 and the general appearance of the spectrum was entirely similar to that of the known complex $[Mo(NO)LI(OCH_2CH_2CH_2Br)]$.[7] The presence of iodine in the 3-iodopropoxide ligand was confirmed by iodine analysis so that (**2**) may be formulated as $[Mo(NO)LI(OCH_2CH_2CH_2I)]$. The pink colour of (**3**) and the observation of ν(NO) at 1 640 cm^{-1} were indicative of a bis(alkoxide) or hydroxy–alkoxide formulation for this *compound. The* 400 MHz ^1H n.m.r. spectrum of (**3**) exhibited signals of relative areas 1:1:1:3:3:6:3:3 at δ 5.87, 5.80, 5.75, 2.57, 2.49, 2.34, 2.33, and 2.32 attributable to the protons in L. This intensity pattern indicates that there is no plane of symmetry in the molecule and rules out a symmetric bis(alkoxide) formulation for (**3**). The remaining signals in the spectrum are consistent with the presence of a ligand of the form $OCH_2CH_2CH_2OCH_2CH_2CH_2X$. The methylene protons adjacent to the alkoxide oxygen appear as an AB pair giving two multiplets of area 1 centred at δ 5.63 and 5.36. The latter signal appears as an overlapping doublet of triplets with $^2J_{AB} = 11$ Hz and $^3J_{AX} = {}^3J_{AY} = 6$ Hz. The former signal appears as a doublet of quartets with $^2J_{BA} = 11$, $^3J_{BX} = 8$, and $^3J_{BY} = 6$ Hz. The other methylene protons adjacent to oxygen or the group X appear as triplets each of relative area 2 at δ 3.68, 3.36, and 3.27 with $^3J_{HH} = 6$ or 7 Hz. The remaining methylene groups appear as two multiplets of area 2 at δ 2.32 and 2.01. The former lies under the signals attributable to the pyrazolyl methyl protons while the latter is clearly resolved as a quintet with $^3J_{HH} = 6$ Hz. On the basis of these spectral data (**3**) may be tentatively assigned the formula $[Mo(NO)L(OH)\{O(CH_2)_3O(CH_2)_3X\}]$. However, definitive evidence for the OH proton in such a molecule is lacking and the elemental analyses do not support this formulation with X = I. Four sets of consistent elemental analysis figures were obtained for C, H, and N. These values fell in the ranges C, 32.8—33.6; H, 4.5—5.3; and N, 13.3—13.5% with average values being C, 33.2; H, 5.1; and N, 13.4%, while iodine analysis gave values of 28.1 and 27.2% on two samples. These figures give an empirical formula containing $C_{21}H_{38.8}I_{1.66}N_{7.3}$ in a compound of molecular weight 759 compared to the expected composition of $C_{21}H_{35}BIMoN_7O_4$ and molecular weight of 682.6 for $[Mo(NO)L(OH)\{(CH_2)_3O(CH_2)_3I\}]$. In the light of these data we are unable to propose a definitive formulation for (**3**) other than to observe that the ^1H n.m.r. data appear to indicate that two molecules of $\overline{O(CH_2)_2CH_2}$ have been linked together in forming this compound. The spectral data also confirm the presence of the $\{Mo(NO)L\}^{2+}$ moiety in (**3**).

The reaction of $[Mo(NO)LI_2]$ with $\overline{OCH_2CHMe}$ afforded a green solution from which both green and pink fractions could be separated by chromatography. As with the products from the reactions with $\overline{O(CH_2)_2CH_2}$, we were unable to characterise the pink fraction definitively. The ^1H n.m.r. spectrum showed that a complex mixture of products was present and this defied all our attempts to effect a separation of the components. The i.r. spectrum of the green fraction, (**4**) contained ν(NO) at 1 670 cm^{-1} in addition to bands attributable to the presence of L. The ^1H n.m.r. spectrum indicated that a mixture of isomers was also present in this material. The complex will necessarily be a mixture of diastereomers as both the molybdenum centre and the alkoxide ligand are chiral. Furthermore the propane ring may open in either of two ways to produce $-OCH_2CHMeX$ or $-OCHMeCH_2X$ as the ligand. Signals attributable to both species could be identified in the spectrum of the green fraction which also contained signals attributable to the presence of L. The ^1H n.m.r. spectrum of $[Mo(NO)LI(OCHMe_2)]$ exhibits a characteristic septet at δ 6.30 due to the unique proton of the isopropyl moiety.[8] The principal component of the green mixture exhibited a 12-line multiplet at δ 6.15 which may be assigned to the unique proton in a $-OCH(Me)CH_2X$ ligand. Another 12-line multiplet was observed at δ 6.00 at two thirds the intensity of the signal at δ 6.15. In addition, signals attributable to the α-methylene protons of a $-OCH_2CH(Me)X$ ligand were present in the region δ 5.35—5.85. The total integration of these amounted to eight ninths the intensity of the signal at δ 6.15. In the methyl region doublets attributable to the alkoxide ligand methyl groups were observed at δ 2.01, 1.95, 1.94, and 1.63 in the relative area ratio 1:3:1:5 with the signal at δ 1.63 integrating at 3:1 with respect to the signal at δ 6.15. These data suggest that there are four components in the mixture in the approximate proportions 5:3:1:1 based on the integration of the alkoxide methyl resonances. The two principal components of the mixture appear to contain the $Mo-OCH(Me)CH_2X$ moiety while the two minor components appear to contain the $Mo-OCH_2CH(Me)X$ moiety as judged by the characteristic signals attributable to protons on the α-carbon of the alkoxide ligand.

After repeated column chromatography and fractional crystallisation we were able to separate the principal component of this mixture from the other materials present. Elemental analyses of the purified (**4**) were consistent with its formulation as $[Mo(NO)LI(OC_3H_6I)]$. The 400 MHz ^1H n.m.r. spectrum of this separated material was superimposable on that of the major component of the mixture obtained initially. The pyrazolyl H^4 protons appeared as three singlets of area 1 at δ 5.88, 5.83, and 5.82 while the methyl protons from L appeared as five singlets of area 3 at δ 2.34, 2.36, 2.38, 2.45, and 2.49. The sixth signal of area 3 at δ 2.40 exhibited a slight splitting of *ca.* 0.3 Hz which may result from the presence of disastereomers. The methyl protons of the alkoxide ligand appeared as a doublet ($^3J_{HH} = 6$ Hz) of area 3 at δ 1.62 which again showed some additional splitting of *ca.* 0.2 Hz. The unique proton of the $Mo-OCH(Me)CH_2I$ moiety appeared as a 12-line multiplet of area 1 at δ 6.15 p.p.m. The methylene protons of the alkoxide ligand appeared as an AB pair giving rise to resonances, each of area 1, at δ 4.33 and 3.29. The signal at δ 4.33 was a quartet with $^2J_{AB} = 10$ Hz and additional coupling to the unique proton with $^3J_{AX} = 4$ Hz. The signal at δ 3.29 appeared as a triplet being a doublet of doublets with $^2J_{BA} = 10$ Hz and $^3J_{BX} = 10$ Hz. Decoupling experiments showed that irradiation of the signal at δ 6.15 collapsed the methyl doublet at δ 1.62 to a singlet, the quartet at δ 4.33 to a doublet with $^2J_{AB} = 10$ Hz and the triplet at δ 3.29 to a doublet with $^2J_{BA} = 10$ Hz. Irradiation at δ 3.29 partially collapsed the signals at δ 4.33 and 6.15, while irradiation at 4.33 collapsed the signal at δ 6.15 to a doublet of quartets with $^3J_{HH} = 6$ Hz and $^2J_{BX} = 10$ Hz, and removed the AB coupling of 10 Hz from the signal at δ 3.29. These results are consistent with the formulation of this separated compound as $[Mo(NO)LI\{OCH(Me)CH_2I\}]$.

Reactions of $[Mo(NO)LI_2]$ *with Tetrahydropyran and Oxacycloheptane.*—The reaction between $[Mo(NO)LI_2]$ and the seven-membered ring heterocycle proceeded over a period of 2 h at reflux to produce a green solution. As with small ring heterocycles both a green and a pink fraction could be separated from the reaction products by chromatography. The pink fraction was obtained as an oil and could not be characterised adequately. The green fraction, (**5**), exhibited bands in its i.r. spectrum consistent with the presence of L along with ν(NO) at 1 670 cm^{-1}. The 100 MHz ^{1}H n.m.r. spectrum exhibited signals attributable to L at δ 5.84, 5.81, 5.78, 2.50, 2.41, 2.38, and 2.35 in the area ratios 1:1:1:3:3:3:9. The α-methylene protons attributable to an alkoxide ligand appeared as a multiplet of area 2 at δ 5.60 and the terminal $-CH_2I$ protons appeared as a signal of area 2 at δ 4.10. The remaining eight protons of the alkoxide ligand appeared as a group of signals in the region δ 0.7—2.0 and were obscured by signals from a molecule of hexane of crystallisation. The presence of iodine in the alkoxide ligand was confirmed by iodine analysis. As with the previous examples the spectroscopic and elemental analysis data support the formulation of (**5**) as an iodoalkoxide, $[Mo(NO)LI\{O(CH_2)_6I\}]$.

The reaction of $[Mo(NO)LI_2]$ with oxacyclohexane (tetrahydropyran) was carried out over a period of 2 d at reflux. Again a green solution was formed and a green product, (**6**), could be isolated by column chromatography. The i.r. spectrum of (**6**) exhibited bands attributable to L in addition to ν(NH) at 3 370 cm^{-1} and ν(NO) at 1 620 cm^{-1}. This low value of ν(NO) was inconsistent with the formulation of (**6**) as an alkoxide and was more in accord with ν(NO) values for 17-electron systems containing the $\{MoL(NO)\}^+$ moiety. This was borne out by the failure of (**6**) to exhibit a ^{1}H n.m.r. spectrum. An e.s.r. spectrum could be obtained in MeCN at room temperature and this showed a signal at $g_{iso.} = 2.002$ with hyperfine coupling of 4.89 mT attributable to ^{95}Mo and ^{98}Mo (15.9 and 9.6% respectively, both with $I = \frac{5}{2}$). These results compare well with those obtained[9] for the 17-electron system $[Mo(NO)LI\{HN(CH_2)_n\}]$ (n = 4 or 5). The elemental analyses of (**6**) are consistent with the formulation $[Mo(NO)LI(3,5\text{-}Me_2C_3N_2H_2)]\cdot 0.5\ CH_2Cl_2$ and the compound is a non-conductor in MeCN solution. This formulation has been confirmed by an *X*-ray diffraction study.[10]

The formation of the 17-electron complex $[Mo(NO)LI(3,5\text{-}Me_2C_3N_2H_2)]$ (**6**) from the reaction between $[Mo(NO)LI_2]$ and tetrahydropyran is surprising. The only source of the 3,5-$Me_2C_3N_2H_2$ ligand is the ligand L and a degradation reaction must be occurring to provide a source of 3,5-$Me_2C_3N_2H_2$ which might then substitute for iodine in the remaining $[Mo(NO)LI_2]$. The degradation of L in reactions of $[Mo(NO)LI_2]$ is not unprecedented. A deboronation reaction to form $[Mo(NO)(1,2\text{-}O_2C_6H_4)(3,5\text{-}Me_2C_3N_2H_2)_3]$ has been observed with catechol.[11] In addition, the reactions between $[Mo(NO)LI_2]$ and 1,2-$(NH_2)(SH)C_6H_4$ or 1,2-$(NH_2)_2C_6H_4$ lead to the loss of one dimethylpyrazole group from L,[12] whilst the reaction with acetone affords the dimethylpyrazolyl containing cation $Me_5C_6H_3N_2(OH)^+$.[13]

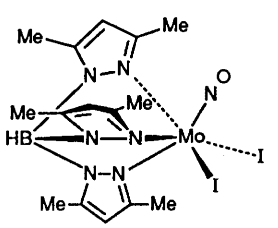
Electrochemical Studies.—The electrochemical properties of the new complexes were investigated by cyclic voltammetry using solutions in MeCN or thf. The alkoxide derivatives, $[Mo(NO)LI\{O(CH_2)_nI\}]$, exhibited irreversible one-electron reductions at −0.64 V [saturated calomel electrode (s.c.e.), MeCN], n = 3; −0.65 V (MeCN), n = 4; and −0.80 V (thf), n = 6. Similar results have been obtained previously[7] with $[Mo(NO)LI(OEt)]$ which exhibited a reduction process at −0.61 V (s.c.e., MeCN). The irreversible nature of the reduction processes found for these complexes may be attributed to I^- dissociation from the reduced species.[7] The complex formulated as $[Mo(NO)LI\{OCH(Me)CH_2I\}]$ similarly exhibited an irreversible reduction process at −0.70 V (thf) while the pink complex (**3**), tentatively formulated as $[Mo(NO)L(OH)\{O(CH_2)_3O(CH_2)_3X\}]$, exhibited an irreversible reduction at −1.26 V (thf) which may be compared with the value of −1.33 V (MeCN) obtained for $[Mo(NO)L\{OCH_2(CH_2OCH_2)_nCH_2O\}]$ (n = 3 or 4).[14]

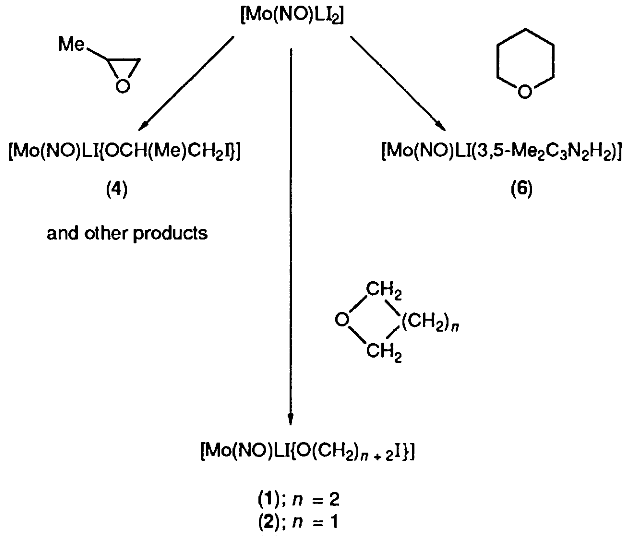
The cyclic voltammogram of $[Mo(NO)LI(3,5\text{-}Me_2C_3N_2H_2)]$ (**6**) exhibited an irreversible one-electron reduction at −1.70 V (MeCN) corresponding to the formation of an unstable 18-electron complex. A reversible one-electron oxidation process was also observed at +0.54 V (MeCN) with a cathodic–anodic peak separation of 80 mV, comparable to the values of 60—80 mV obtained with ferrocene. This latter process corresponds with the formation of the 16-electron complex $[Mo(NO)LI(3,5\text{-}Me_2C_3N_2H_2)]^+$ which could be formed by substitution of I^- in $[Mo(NO)LI_2]$ by 3,5-$Me_2C_3N_2H_2$. The reduction potential of this complex is such that, if formed, it would be reduced by I^- to the neutral 17-electron system isolated from the reaction between tetrahydropyran and $[Mo(NO)LI_2]$. The electrochemical data we have obtained are in accord with the formulation of the principal green products from the reactions between $[Mo(NO)LI_2]$ and $\overline{OCH_2CHMe}$ and $\overline{O(CH_2)_nCH_2}$ (n = 2, 3, or 5) as monoalkoxide derivatives. The data for $[Mo(NO)LI(3,5\text{-}Me_2C_3N_2H_2)]$ indicate that this compound, which is isolated as a 17-electron complex, may be oxidised to a 16-electron species and irreversibly reduced to an 18-electron species. This contrasts with the behaviour of $[Mo(NO)L(NC_5H_5)_2]^+$ which is reversibly reduced to an 18-electron complex but does not exhibit simple oxidation processes corresponding with the formation of a 16-electron complex.

Discussion

The Lewis acid promoted cleavage of cyclic ethers is a well established reaction of considerable synthetic importance.[15] However, reports of the isolation of transition-metal alkoxides from reactions between metal halides and cyclic ethers are rare. There are certainly indications that such reactions may occur and the reaction between $FeCl_3$ and oxacyclopropane, for example, has been found to afford materials formulated as chloro–bis(alkoxy) complexes of Fe^{III}.[16] Similarly, a complex formulated as $BrCH_2CH_2OMgBr\cdot OEt_2$ has been isolated from the reaction between ethylene oxide and $MgBr_2$ in diethyl ether.[17] Unfortunately the lability, and sensitivity to hydrolysis, of such compounds makes their isolation and characterisation difficult. This is especially so when a variety of products are formed in the reaction. More tractable products are obtained when halides of elements forming relatively stable alkoxide derivatives are used. Thus derivatives such as $AsCl(OCH_2CHClMe)_2$ may be isolated[18] from the reactions of oxirans with Group 5 element chlorides. More recently an example of ring opening and alkoxide formation has been reported in the reaction between $ZrCl_4$ and the cyclic polyether 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6).[19] In this case the product was shown by an *X*-ray diffraction study to be $[ZrCl_2\{OCH_2(CH_2OCH_2)_5CH_2Cl\}]^+$. The larger ring size cyclic ethers are less reactive than epoxides but can exhibit similar ring opening reactions in the presence of Lewis acids. The presence of CuI promotes the ring opening of 2-methyltetrahydrofuran or oxacyclobutane by alkyl-lithium reagents,[20] while $ZnBr_2$ promotes the opening of thf in acetic anhydride at temperatures of 190 °C or above.[21] The acetylation of thf can also be effected under more mild conditions and, using $MgBr_2$, a 97% yield of $MeCO_2(CH_2)_4Br$ could be obtained from a mixture of thf, $(MeCO)_2O$, and $MgBr_2$ in acetonitrile after 12 h at room temperature.[22] Oxacyclohexane proved to be less reactive than thf and in a similar reaction a 50% yield of $MeCO_2(CH_2)_5Br$ was obtained after 15 h at 85 °C.

The reactions between $[Mo(NO)LI_2]$ and cyclic ethers reported here, and summarised in the Scheme, are qualitatively similar to the previously reported cleavage reactions in that a metal dihalide derivative is involved. If the reaction products were to be treated with aqueous acid, the hydrolysis of the product alkoxide would lead to the reformation of the metal





Scheme.

dihalide, or possibly a hydroxide, and the release of the cleaved cyclic ether as $HO(CH_2)_nI$ (n = 3, 4, or 6).[1] However, under non-aqueous conditions, the unusual stability of alkoxide derivatives of $[Mo(NO)L]^{2+}$ has allowed the isolation of what are effectively intermediates in the metal promoted cleavage reactions of the cyclic ethers. We are not in a position to define the mechanism of the cleavage reaction with certainty but some comment on the possible course of the reaction may be made. It was noted earlier that $[Mo(NO)LI_2]$ did not react with rigorously dried thf. However, in the presence of moisture the reaction to form the alkoxide derivative proceeds smoothly. Other studies have shown that, in moist thf, $[Mo(NO)LI_2]$ reacts to produce a paramagnetic species which may be formulated[3] as $[Mo(NO)LI(thf)]$. The sequence of reactions involved may be summarised as follows $[\{Mo\} = Mo(NO)L]$.

$$[\{Mo\}I_2] + H_2O \longrightarrow [\{Mo\}I(OH)] + HI \quad (1)$$

$$[\{Mo\}I_2] + HI \longrightarrow [\{Mo\}I_2]^- + H^+ + 0.5\, I_2 \quad (2)$$

$$[\{Mo\}I_2]^- + \text{thf} \longrightarrow [\{Mo\}I(\text{thf})] + I^- \quad (3)$$

Attack of I^- on the co-ordinated thf might then effect a ring opening reaction leading to alkoxide formation. The product $[\{Mo\}I\{O(CH_2)_4I\}]^-$ would be a powerful reducing agent[7] which would be oxidised readily to the isolated product, (**1**), according to equation (4), by the iodine produced in equation (2).

$$[\{Mo\}I\{O(CH_2)_4I\}]^- + I_2 \longrightarrow [\{Mo\}I\{O(CH_2)_4I\}] + I^- \quad (4)$$

An alternative possibility is that $[\{Mo\}I(\text{thf})]$ is oxidised by iodine prior to I^- attack according to equations (5) and (6).

$$I_2 + [\{Mo\}I(\text{thf})] \longrightarrow I^- + [\{Mo\}I(\text{thf})]^+ \quad (5)$$

$$[\{Mo\}I(\text{thf})]^+ + I^- \longrightarrow [\{Mo\}I\{O(CH_2)_4I\}] \quad (6)$$

However, the oxidation potential of $[Mo(NO)LI(thf)]$ is reported[3] to be +0.66 V (*vs.* s.c.e.) so that this reaction could not be fully effected by the I_2–I^- couple with a potential of +0.48 V.

A second reaction sequence may be proposed which does not involve the reaction of co-ordinated thf. This requires the cleavage of free cyclic ether by the HI liberated according to equation (2). The resulting iodoalcohol may then react with $[Mo(NO)LI_2]$ to produce the alkoxide product, which is isolated, and regenerate a molar equivalent of HI. In this context it is noteworthy that the initial product from the reaction between $[Mo(NO)LI_2]$ and $\overline{\mathrm{OCH_2C}}\mathrm{HMe}$ was found to be a mixture of products which appeared to contain the ligands $-OCH(Me)CH_2I$ and $-OCH_2CH(Me)I$ in the approximate ratio 8:2. The opening of $\overline{\mathrm{OCH_2C}}\mathrm{HMe}$ by HI in water at 65 °C similarly affords[23] 82% 1-iodopropan-2-ol and 18% 2-iodopropan-1-ol in an overall yield of 75%. It would appear that, if I^- attack on co-ordinated propene oxide is involved, the product isomer distribution remains similar to that found with HI alone or with HBr in the presence of $MgBr_2$.

One objection to the proposal that ring opening is effected by free HI is the rapidity of the reactions with $\overline{\mathrm{O(CH_2)_2CH_2}}$ and $\overline{\mathrm{OCH_2C}}\mathrm{HMe}$. The reaction of $[Mo(NO)LI_2]$ with alcohols used in a large excess as the solvent takes hours at elevated temperatures, unless a halide abstractor or base is added.[7,8] It would be surprising if substoicheiometric quantities of alcohol could produce significant yields of alkoxide within 1 h as found with $\overline{\mathrm{OCH_2C}}\mathrm{HMe}$ and $\overline{\mathrm{O(CH_2)_2CH_2}}$. A similar argument may be used against a cleavage reaction involving radical intermediates as shown in equations (7) and (8), although the direct reaction of a radical intermediate with $[Mo(NO)LI_2]$ cannot be ruled out.

$$\overline{\mathrm{O(CH_2)_nCH_2}} + [\{Mo\}I_2] \longrightarrow {}^{+\bullet}\overline{\mathrm{O(CH_2)_nCH_2}} + [\{Mo\}I_2]^- \quad (7)$$

$${}^{+\bullet}\overline{\mathrm{O(CH_2)_nCH_2}} + 2HI \longrightarrow HO(CH_2)_nCH_2I + H^+ + I_2 \quad (8)$$

In view of the effectiveness of the labile redox inert Mg^{2+} centre derived from $MgBr_2$ in promoting the cleavage of cyclic ethers the direct reaction of I^- with co-ordinated thf remains an attractive proposition for rationalising the reactivity of $[Mo(NO)LI_2]$ towards cyclic ethers. The redox properties of the $\{Mo(NO)\}^{3+}$ centre are not expressed in the cleavage reaction itself but are probably important in, first, labilising I^- and, secondly, forming the 16-electron alkoxide stabilised by O→Mo $p \rightarrow d$ charge donation. In this context we have found that $[Mo(NO)LCl_2]$ does not react with moist thf under similar conditions and this may be rationalised by the inability of Cl^- to reduce $[\{Mo\}Cl_2]$ and labilise the halide as the initiating step in the ether cleavage reaction.

A puzzling feature of the chemistry described here is the formation of $[Mo(NO)LI(3,5\text{-}Me_2C_3N_2H_2)]$ in the reaction with oxacyclohexane. The other four cyclic ethers studied produced alkoxides as the principal reaction products. The only explanation we are able to offer for this observation is that oxacyclohexane is the reagent least susceptible to ring opening by cleavage of the ether group. The five- and six-membered ring systems are the most stable of those studied and the higher stability of oxacyclohexane compared to thf is manifest in the more forcing conditions required for its acetylation by $(\mathrm{MeCO})_2\mathrm{O}$ in the presence of $\mathrm{MgBr_2}$ as mentioned earlier.[22] It would appear, therefore, that the ring opening reaction with tetrahydropyran may be sufficiently slow that an alternative reaction involving L may take place instead. In all the reactions leading to alkoxides only 50—80% of the $[\mathrm{Mo(NO)LI_2}]$ used was recovered in the form of green, and in some cases, pink products shown to contain L. Thus the reactions can in no way be regarded as stoicheiometric and other intractable products were also formed. In the case of tetrahydropyran the paramagnetic complex (**6**) was the dominant product and thus isolated more readily. Even so the yield of this material was only 54% taking into account the consumption of 25% of the starting material to provide stoicheiometric 3,5-$\mathrm{Me_2C_3N_2H_2}$ for reaction with the remaining 75%. Despite the complicated nature of the reactions described here, they have provided unusual examples of the formation of transition-metal alkoxides from cyclic ethers, and of the iodination of organic substrates by $[\mathrm{Mo(NO)LI_2}]$.

Experimental

Synthetic Studies.—The compound $[\mathrm{Mo(NO)LI_2}]\cdot\mathrm{C_6H_5Me}$ was prepared according to the literature method;[24] other commercial reagents were used as supplied. Tetrahydrofuran was dried by distillation from sodium diphenylketyl where necessary and MeCN for electrochemistry was redistilled from $\mathrm{CaH_2}$. All reactions were carried out under nitrogen but purification procedures were carried out in air. Column chromatography was performed on 3 × 40 cm columns of silica gel Merck 70—230 ASTM. Elemental analyses were carried out by the Microanalytical Laboratory, University of Birmingham.

I.r. spectra were recorded using a PE 297 spectrometer with samples as KBr discs. 400 MHz Proton n.m.r. spectra were obtained from solutions in $\mathrm{CDCl_3}$ using a Bruker WH400 spectrometer of the SERC high-field n.m.r. service at Warwick University; all chemical shifts are reported against $\mathrm{SiMe_4}$ (δ 0). E.s.r. spectra were obtained from fluid solutions in $\mathrm{CH_2Cl_2}$ using a Hilger-Watts Microspin *X*-band spectrometer with a 100 MHz modulation (iodo complexes); *g* values were obtained from frequency measurements with a proton-resonance head. Diphenylpicrylhydrazyl was used as the reference. Cyclic voltammetric measurements were made using a Hitek PPR 1 waveform generator and DT 2101 potentiostat or a PAR 174A polarograph. Solutions in MeCN or thf were *ca.* 10^{-3} mol dm^{-3} in the complex and 0.2 mol dm^{-3} in $[\mathrm{NBu^t_4}]\mathrm{BF_4}$ as the base electrolyte. A Pt bead test electrode was used with an s.c.e. reference electrode and ferrocene standard. Potentials are quoted relative to the s.c.e. and under these conditions E_f for the oxidation of ferrocene was found to be 0.42 V. The number of electrons involved in the electrode processes was estimated to be one by comparison with $[\mathrm{Mo(NO)LCl_2}]$.

$[\mathrm{Mo(NO)LI\{OCH(Me)CH_2I\}}]$ (**4**). A solution of $[\mathrm{Mo(NO)LI_2}]\cdot\mathrm{C_6H_5Me}$ (1.0 g, 1.3 mmol) in methyloxacyclopropane (40 cm^3) was refluxed for 1 h, the resulting green solution was filtered, and the solvent removed *in vacuo*. The solid obtained was purified by column chromatography using $\mathrm{CH_2Cl_2}$ to elute the principal green product and 5% thf in $\mathrm{CH_2Cl_2}$ to elute the second pink fraction. Recrystallisation from $\mathrm{CH_2Cl_2}$–hexane was used to purify these reaction products further. The green material was isolated as a microcrystalline solid which proved to contain a mixture of isomers (0.48 g, 44%) (Found: C, 29.8; H, 3.7; I, 34.2; N, 13.3. $\mathrm{C_{18}H_{28}BI_2MoN_7O_2}$ requires C, 29.4; H, 3.8; I, 34.6; N, 13.3%); $\nu_{\mathrm{max.}}$(NO) 1 670 cm^{-1} (KBr); δ_{H}(400 MHz, $\mathrm{CDCl_3}$) 5.880, 5.825, 5.820 (3 × 1 H, 3 × s, $\mathrm{Me_2C_3N_2}\mathit{H}$); 2.490, 2.448, 2.378, 2.363, 2.337, 2.403 [6 × 3 H, 6 × s, $(\mathrm{C}\mathit{H}_3)_2\mathrm{C_3N_2H}$]; 1.618 [3 H, d, ^3J(HH) 6 Hz, $\mathrm{OCH(C}\mathit{H}_3\mathrm{)CH_2I}$]; 6.145 [1 H, m, $\mathrm{OC}\mathit{H}\mathrm{(Me)CH_2I}$]; 4.325 and 3.290 [1 H, q, ^2J(HH) 10, ^3J(HH) 4 Hz, 1 H, t, ^2J(HH) 10, ^3J(HH) 10 Hz, $\mathrm{OCH(Me)C}\mathit{H}_2\mathrm{I}$]. The second fraction was obtained as a pink powder (0.25 g) of uncertain formulation.

$[\mathrm{Mo(NO)LI(OCH_2CH_2CH_2I)}]$ (**2**). A solution of $[\mathrm{Mo(NO)LI_2}]\cdot\mathrm{C_6H_5Me}$ (1.0 g, 1.3 mmol) in oxacyclobutane (20 cm^3) was stirred at room temperature for 10 min. The resulting green solution was filtered and the solvent evaporated *in vacuo*. The solid obtained was separated into green and pink fractions according to the method described for the preceding reaction. The green product was obtained as a microcrystalline solid (0.42 g, 39%) (Found: C, 30.1; H, 4.2; I, 33.2; N, 13.3. $\mathrm{C_{18}H_{28}BI_2MoN_7O_2}$ requires C, 29.4; H, 3.8; I, 34.6; N, 13.3%); $\nu_{\mathrm{max.}}$(NO) 1 670 cm^{-1} (KBr); δ_{H}(400 MHz, $\mathrm{CDCl_3}$) 5.887, 5.846, 5.825 (3 × 1 H, 3 × s, $\mathrm{Me_2C_3N_2}\mathit{H}$); 2.496, 2.416, 2.405, 2.372, 2.368, 2.352 (6 × 3 H, 6 × s, $(\mathrm{C}\mathit{H}_3)_2\mathrm{C_3N_2H}$]; 5.618 [2 H, m, ^2J(HH) 12, ^3J(HH) 6 Hz, $\mathrm{OC}\mathit{H}_2\mathrm{(CH_2)_2I}$], 3.30 [2 H, m, $\mathrm{O(CH_2)_2C}\mathit{H}_2\mathrm{I}$], and 2.45 [2 H, m, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{CH_2I}$]. The second fraction was obtained as a pink powder (0.18 g) of uncertain formulation.

$[\mathrm{Mo(NO)LI\{O(CH_2)_4I\}}]$ (**1**). A solution of $[\mathrm{Mo(NO)LI_2}]\cdot\mathrm{C_6H_5Me}$ (0.5 g, 0.65 mmol) in thf (100 cm^3) was refluxed for 3 d during which time the solution became green. The solvent was removed by evaporation *in vacuo* and the crude product obtained was purified by column chromatography using thf as eluant. The principal green band was collected and purified further by recrystallisation from $\mathrm{CH_2Cl_2}$–hexane (0.42 g, 77%) (Found: C, 30.8; H, 4.1; I, 32.2; N, 13.3. $\mathrm{C_{19}H_{30}BI_2MoN_7O_2}$ requires C, 30.4; H, 4.0; I, 33.9; N, 13.1%); $\nu_{\mathrm{max.}}$(NO) 1 670 cm^{-1} (KBr); δ_{H}(400 MHz, $\mathrm{CDCl_3}$) 5.895, 5.855, 5.835 (3 × 1 H, 3 × s, $\mathrm{Me_2C_3N_2}\mathit{H}$); 2.508, 2.435, 2.415, 2.382, 2.364, 2.358 [6 × 3 H, 6 × s, $(\mathrm{C}\mathit{H}_3)_2\mathrm{C_3N_2H}$]; 5.605, (2 H, m, $\mathrm{OCH_2}$–), 3.240 (2 H, m, –$\mathrm{CH_2I}$), and 2.030 [4 H, m, $\mathrm{OCH_2(C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{)CH_2I}$].

$[\mathrm{Mo(NO)LI(3,5\text{-}Me_2C_3N_2H_2)}]$ (**6**). A solution of $[\mathrm{Mo(NO)LI_2}]\cdot\mathrm{C_6H_5Me}$ (1 g, 1.3 mmol) in oxacyclohexane (50 cm^3) was refluxed for 2 d during which time the solution became green. The reaction mixture was then filtered and the solvent removed from the filtrate by evaporation *in vacuo*. The crude product so obtained was then purified by column chromatography using $\mathrm{CH_2Cl_2}$ as the eluant, the principal green band being collected. Further purification was effected by recrystallisation from $\mathrm{CH_2Cl_2}$–hexane (0.4 g, 54%) (Found: C, 36.3; H, 4.0; N, 18.1. $\mathrm{C_{20}H_{30}BIMoN_9O\cdot0.05CH_2Cl_2}$ requires C, 35.8; H, 4.5; N, 18.3%); $\nu_{\mathrm{max.}}$(NO) 1 620, $\nu_{\mathrm{max.}}$(NH) 3 370 cm^{-1} (KBr); $g_{\mathrm{iso.}}$ 2.002, $A_{\mathrm{iso.}}$ 4.89 mT.

$[\mathrm{Mo(NO)LI\{O(CH_2)_6I\}}]$ (**5**). A solution of $[\mathrm{Mo(NO)LI_2}]\cdot\mathrm{C_6H_5Me}$ (1.0 g, 1.3 mmol) in oxacycloheptane (40 cm^3) was refluxed for 2 h during which time the solution became green. The solvent was then removed by evaporation *in vacuo* and the residual solid purified by column chromatography using $\mathrm{CH_2Cl_2}$ to elute a green fraction and 5% thf in $\mathrm{CH_2Cl_2}$ to elute a pink fraction which proved to be an oil. The green fraction was purified further by recrystallisation from $\mathrm{CH_2Cl_2}$–hexane to give a green powder (0.5 g, 39%) (Found: C, 38.3; H, 5.1; I, 30.0; N, 13.4. $\mathrm{C_{21}H_{34}BI_2MoN_7O_2}$ requires C, 37.6; H, 5.4; I, 29.4; N, 11.4%); $\nu_{\mathrm{max.}}$(NO) 1 670 cm^{-1} (KBr); δ_{H}(100 MHz, $\mathrm{CDCl_3}$) 5.84, 5.81, 5.78 (3 × 1 H, 3 × s, $\mathrm{Me_2C_3N_2}\mathit{H}$); 2.50, 2.41, 2.38, 2.35 [3 × 3 H, 3 × s, 9 H, s, $(\mathrm{C}\mathit{H}_3)_2\mathrm{C_3N_2H}$], 5.60 (2 H, m, $\mathrm{OCH_2}^-$), 4.10 (2 H, m, –$\mathrm{CH_2I}$), and 0.7—2.0 [8 H, m, $\mathrm{OCH_2(C}\mathit{H}_2\mathrm{)_4CH_2I}$].

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