Ring-opening Reactions of Oxacyclobutane with $[M(NO)\{HB(3,5-Me_2C_3HN_2)_3\}X_2]$ (M = Mo, X = Cl or Br; M = W, X = Cl)

Emma M. Coe,[a] **Christopher J. Jones** *,[a] **and Jon A. McCleverty**[b]
[a] *School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK*
[b] *School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK*

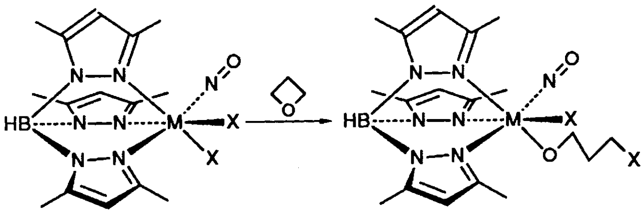
The complexes $[M(NO)LX_2]$ [$L = HB(3,5-Me_2C_3HN_2)_3$; M = Mo, X = Cl or Br; M = W, X = Cl] react with oxacyclobutane to give $[M(NO)L(X)\{O(CH_2)_3X\}]$. The dibromo-complex is the most reactive and may be prepared from the reaction between $[Mo(NO)LI_2]$ and CBr_4.

The ring opening of the cyclic ethers in the presence of Lewis acids is well known and a variety of metal ions are effective in promoting this reaction.[1–7] Despite this, examples of reactions between cyclic ethers and transition-metal halides which lead to well characterised complexes containing halogenated alkoxide ligands are rare. Alkoxide complexes are formed in the reaction between $FeCl_3$ and ethylene oxide,[8] and the reaction between $ZrCl_4$ and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) has been found to give the salt $[ZrCl_2\{(OCH_2CH_2)_5OCH_2CH_2Cl\}][ZrCl_5(thf)]$ (thf = tetrahydrofuran), in which the monocation contains a hexaoxaalkoxy ligand bearing a terminal chloro substituent.[9] More recently we have reported cyclic ether ring opening by what might be regarded as a low-oxidation-state molybdenum halide complex.[10] The formally molybdenum(II) complex $[Mo(NO)LI_2]$ [$L = HB(3,5-Me_2C_3HN_2)_3$] reacts with oxa-cyclobutane, -cyclopentane or -cycloheptane to give the corresponding iodonated alkoxide complexes $[Mo(NO)L(I)\{O(CH_2)_nI\}]$ (n = 3, 4 or 6). The reaction with oxacyclohexane did not afford an alkoxide complex but instead produced $[Mo(NO)L(I)(Me_2C_3H_2N_2)]$ through a degradation of the part of the $[Mo(NO)LI_2]$ present.[10]

In an extension of this work we have investigated the reactions of the other dihalides $[M(NO)LX_2]$ (M = Mo, X = Cl or Br; M = W, X = Cl) with oxa-cyclobutane and -cyclopentane in a qualitative evaluation of the effect of varying the $\{MX_2\}$ moiety on the reactivity of $[M(NO)LX_2]$ towards cyclic ethers.

Results and Discussion

Previously we found that the smaller-ring-size cyclic ethers methyloxacyclopropane (propylene oxide) and oxacyclobutane react rapidly with $[Mo(NO)LI_2]$. Oxacyclopentane reacts slowly in the presence of moisture but not under dry conditions and oxacyclohexane does not afford an alkoxy complex.[10] Accordingly oxa-cyclobutane and -cyclopentane were selected as the best reagents to assess the reactivities of $[M(NO)LX_2]$ (M = Mo, X = Cl or Br; M = W, X = Cl) towards cyclic ethers. The progress of the reactions was monitored using thin-layer chromatography and the major reaction products were separated by chromatography and characterised by elemental analyses and by IR, ^1H NMR and mass spectroscopy. Since we have recently experienced problems with the use of NOX (X = Cl or Br) to prepare $[Mo(NO)LX_2]$ a new method of preparing $[Mo(NO)LBr_2]$ was used. This involves the reaction of $[Mo(NO)LI_2]$, which can be reliably prepared[11] from $[Mo(NO)L(CO)_2]$, with CBr_4 and affords $[Mo(NO)LBr_2]$ in *ca.* 50% yield.



Scheme 1

As with $[Mo(NO)LI_2]$, the complexes $[M(NO)LX_2]$ failed to react with dry oxacyclopentane and could be recovered unchanged even after being heated under reflux for 1 week under dinitrogen. When the solutions were exposed to moisture reactions did occur but the products were not found to contain alkoxide ligands. Instead hydrolysis or degradation of the complex occurred.

Complexes of formula $[M(NO)L(X)\{O(CH_2)_3X\}]$ (M = Mo, X = Cl or Br; M = W, X = Cl) were obtained in moderate yields from the reactions between the corresponding metal dihalide and oxacyclobutane (Scheme 1). These complexes were formed from reactions with undried oxacyclobutane since traces of moisture promote reactions of the dihalide complexes.[12] The reaction with $[Mo(NO)LBr_2]$ proceeded to completion, as judged by TLC, over a period of 4 h at room temperature. This may be compared with the reaction time of 30 min needed to produce $[Mo(NO)L(I)\{O(CH_2)_3I\}]$ under similar conditions. In the case of $[M(NO)LCl_2]$ (M = Mo or W) it was necessary to heat the reaction mixture to effect the ether cleavage and the tungsten complex reacted more slowly than its molybdenum counterpart.

The new complexes exhibit characteristic stretching frequencies attributable to the presence of the ligand L including ν(BH) at 2550 cm^{-1}. The appearance of $\nu_{max}(NO)$ at approximately 1670 cm^{-1} in each case is consistent with the formation of an alkoxide halide complex.[13] The mass spectra contain molecular ions in addition to ions at $M - 30$ due to the loss of NO and other fragment ions which are consistent with the proposed formulations. The 270 MHz ^1H NMR spectra are also consistent with the formulations proposed. They contain three signals, each of relative area 1, in the region δ 5.7–5.9 attributable to the pyrazolyl H^4 protons and six signals, each of relative area 3 in the region δ 2.3–2.5 attributable to the pyrazolyl methyl groups. The α-methylene protons of the alkoxide ligand appear as multiplets of relative area 2 in the region δ 5.6–6.0, this low-field shift being typical of complexes of the general formula $[Mo(NO)L(X)(OR)]$ (R = hydrocarbyl).[13]

Triplets of area 2 attributable to the terminal CH_2X groups are seen in the region δ 3.2–3.7 and the β-CH_2 methylene protons are observed as multiplets at about δ 2.

The previous work has shown that the more highly strained three- and four-membered ring cyclic ethers react more rapidly with $[Mo(NO)LI_2]$ than the five-, six- or seven-membered ring cyclic ethers. The results described here indicate that, on a qualitative basis, the reactivities of $[M(NO)LX_2]$ towards oxacyclobutane decrease with M–X combinations in the order Mo–I > Mo–Br > Mo–Cl > W–Cl. Among these compounds only the most reactive, $[Mo(NO)LI_2]$, reacts with oxacyclopentane to form an alkoxide complex.

Experimental

Commercial reagents and solvents were used as supplied except for oxacyclopentane which was distilled from sodium–benzophenone and toluene which was purified and dried by distillation from sodium. The complexes $[M(NO)LCl_2]$ (M = Mo or W) were prepared using previously reported methods,[11,14,15] but an alternative method was devised for the synthesis of $[Mo(NO)LBr_2]$ and is described below. Reactions were carried out under dry dinitrogen, unless otherwise stated, but the products were isolated in air.

Infrared spectra were recorded from KBr discs using a Perkin-Elmer model 297 spectrometer, electron-impact mass spectra on a Kratos MS80RF instrument and ^1H NMR spectra from $CDCl_3$ solutions using a JEOL JNM GX270 spectrometer with $SiMe_4$ as reference (δ 0). Elemental analyses were performed by the Microanalytical Service, School of Chemistry, University of Birmingham.

$[Mo(NO)\{HB(Me_2C_3N_2H)_3\}Br_2]$.—A solution of $[Mo(NO)\{HB(Me_2C_3N_2H)_3\}I_2]\cdot PhMe$ (2.995 g, 4.42 mmol) and CBr_4 (4.410 g, 13.3 mmol) in toluene (100 cm^3) was stirred under reflux for 3 d. The solution was then cooled, filtered and evaporated to dryness under reduced pressure. The solid residue was recrystallised from toluene (≈50 cm^3) and dried *in vacuo* affording the product as a red-brown solid (1.335 g, 52%) (Found: C, 31.1; H, 3.8; N, 17.0%; M^+, 583. $C_{15}H_{22}BBr_2MoN_7O$ requires C, 30.9; H, 3.8; N, 16.8%; *M*, 583); ν_{max}/cm^{-1}(NO) 1700s; $\delta_H(CDCl_3)$ 2.33, 2.37, 2.44 and 2.57 [6 H, s; 6 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$], 5.90 and 5.95 [1 H, s; 2 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 583 (M^+), 553 (*M* − NO), 504 (*M* − Br) and 474 (*M* − NO, Br).

$[Mo(NO)\{HB(Me_2C_3N_2H)_3\}Cl\{O(CH_2)_3Cl\}]$.—The complex $[Mo(NO)\{HB(Me_2C_3N_2H)_3\}Cl_2]$ (0.248 g, 0.50 mmol) and oxacyclobutane (3 cm^3) were stirred for 2 h at room temperature (r.t.) then heated under reflux for 3 h. The reaction mixture was evaporated to dryness under reduced pressure and the solid residue purified by column chromatography on silica gel using dichloromethane as the eluent. The major blue-green band was collected and a turquoise product was isolated (0.15 g, 54%) (Found: C, 39.1; H, 5.2; N, 18.0%; M^+, 553. $C_{18}H_{28}BCl_2MoN_7O_2$ requires C, 39.2; H, 5.1; N, 17.8%; *M*, 552); ν_{max}/cm^{-1}(NO) 1670s; $\delta_H(CDCl_3)$ 2.32, 2.36, 2.37, 2.38, 2.44 and 2.51 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$], 2.32–2.56 (2 H, m, CH_2), 3.72, 3.75 and 3.77 (2 H, t, CH_2Cl), 5.76, 5.87 and 5.92 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)$], 5.91–5.61 (2 H, m, $MoOCH_2$); *m/z* 553 (M^+), 523 (*M* − NO) and 446 [*M* − NO − $(CH_2)_3Cl$].

$[Mo(NO)\{HB(Me_2C_3N_2H)_3\}Br\{O(CH_2)_3Br\}]$.—This compound was prepared and purified in a similar manner to that for $[Mo(NO)\{HB(Me_2C_3N_2H)_3\}Cl\{O(CH_2)_3Cl\}]$ using $[Mo(NO)\{HB(Me_2C_3N_2H)_3\}Br_2]$ (0.252 g, 0.43 mmol), oxacyclobutane (5 cm^3) and a reaction time of 4 h at r.t. A green product was isolated (0.147 g, 53%) (Found: C, 34.0; H, 4.7; N, 15.1%; M^+, 643. $C_{18}H_{28}BBr_2MoN_7O_2$ requires C, 33.7; H, 4.4; N, 15.3%; *M*, 641); ν_{max}/cm^{-1}(NO) 1670s; $\delta_H(CDCl_3)$ 2.36, 2.37, 2.38, 2.41 and 2.51 [3 H, s; 6 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$], 2.32–2.53 (2 H, m, CH_2), 3.55, 3.57 and 3.60 (2 H, t, CH_2Br), 5.79, 5.86 and 5.91 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)$], 5.79–5.96 (2 H, m, $MoOCH_2$); *m/z* 643 (M^+), 613 (*M* − NO) and 490 [*M* − NO − $(CH_2)_3Br$].

$[W(NO)\{HB(Me_2C_3N_2H)_3\}Cl\{O(CH_2)_3Cl\}]$.—This compound was prepared and purified in a similar manner to that for $[Mo(NO)\{HB(Me_2C_3N_2H)_3\}Cl\{O(CH_2)_3Cl\}]$ using $[W(NO)\{HB(Me_2C_3N_2H)_3\}Cl_2]$ (0.252 g, 0.43 mmol), oxacyclobutane (3 cm^3) and a reaction time of 2 d at r.t. followed by 3 h under reflux. A purple product was isolated (0.057 g, 21%) (Found: C, 33.5; H, 4.4; N, 15.6%; M^+, 641. $C_{18}H_{28}BCl_2N_7O_2W$ requires C, 33.8; H, 4.4; N, 15.3%; *M*, 640); ν_{max}/cm^{-1}(NO) 1630s; $\delta_H(CDCl_3)$ 2.347, 2.353, 2.37, 2.40, 2.57 and 2.58 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3, H, s; 3 H, s, $(Me_2C_3N_2H)_3$], 2.29–2.60 (2 H, m, CH_2), 3.70, 3.72 and 3.75 (2 H, t, CH_2Cl), 5.83, 5.87 and 5.94 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 5.83–5.98 (2 H, m, $WOCH_2$); *m/z* 641 (M^+) and 611 (*M* − NO).

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