Some Reactions of Cationic 16-Electron Molybdenum Mononitrosyl Complexes with Phenols and Arylamines

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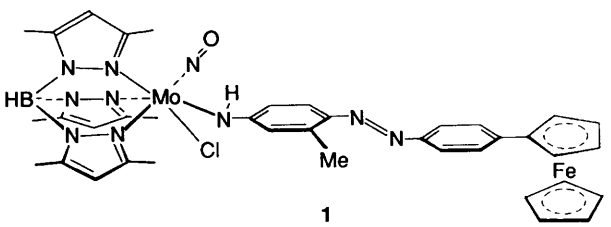
The complex $[Mo(NO)LCl_2]PF_6$ (L = *N,N′, N″*-trimethyl-1,4,7-triazacyclononane) reacts with methanol to give $[Mo(NO)L(Cl)(OMe)]PF_6$ but the reaction with 4-ferrocenylphenol results in reduction rather than phenoxide formation. The complex $[Mo(NO)LBr_2]PF_6$ reacts with 4-amino-2-methyl-4′-ferrocenylazobenzene to give a bimetallic complex containing a seven-co-ordinate paramagnetic molybdenum centre (μ_{eff} = 3.13).

Recent interest in molecular materials which might exhibit substantial non-linear optical (n.l.o.) properties[1,2] has led to the discovery of some transition metal-containing compounds which exhibit substantial second harmonic generation (s.h.g.) indicative of second-order n.l.o. properties.[3-5] In order for a molecular material to exhibit second-order n.l.o. properties it is necessary for the molecule to be dipolar and polarisable and to crystallise in a non-centrosymmetric space group, otherwise symmetry requires that the second-order electric susceptibility, $X^{(2)}$, of the material is zero. Since the molecular packing cannot usually be predicted this aspect in the design of molecular n.l.o. materials is often left to chance.

We have previously used a 16-electron molybdenum mononitrosyl moiety as the acceptor group in dipolar molecules, some of which exhibit substantial s.h.g.[4] The most active of the compounds studied contain a sterically bulky ferrocenyl donor group linked to the molybdenum by a diazadiaryl bridge as in complex **1** for example.[4] Replacement of the ferrocenyl group by less bulky donors such as OMe or NMe_2 generally results in materials which do not show significant s.h.g.[5] Since these molecules should also have the necessary electronic properties to exhibit s.h.g. it seems likely that unfavourable molecular packing is responsible for their inactivity. One strategy which may be used to exercise some control over packing is to prepare salts in which the nature of the counter ion may be varied to change the packing arrangement of the polarisable component. This approach has been applied with considerable success in some cases leading to very large relative harmonic intensities for s.h.g.[6,7] In seeking to apply this strategy to the molybdenum mononitrosyl systems we have investigated the derivative chemistry of known cationic molybdenum mononitrosyl complexes $[Mo(NO)LX_2]PF_6$ (L = *N,N′,N″*-trimethyl-1,4,7-triazacyclononane; X = Cl or Br)[8-10] with a view to obtaining cationic analogues of the neutral derivatives of $[Mo(NO)\{HB(3,5\text{-}Me_2C_3HN_2)_3\}X_2]$ studied previously.[4,5]



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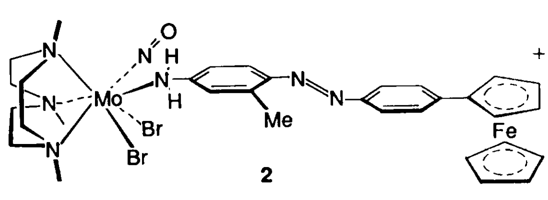

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Experimental

Commercial reagents were used as supplied and $[Mo(NO)LX_2]PF_6$ (X = Cl or Br)[9] and 4-amino-2-methyl-4′-ferrocenylazobenzene[10-12] were prepared using previously described methods. Solvents were dried using standard methods and reactions were carried out under an atmosphere of dinitrogen.

Infrared, 270 MHz ^1H NMR and mass spectra were measured using Perkin-Elmer PE297, JEOL GX270 and Kratos MS80RF instruments respectively. Electrochemical measurements were performed using a PAR174A potentiostat and a platinum-bead electrode. Solutions were *ca.* 10^{-3} mol dm^{-3} in the compound and 0.2 mol dm^{-3} in $[NBu_4]BF_4$ as the supporting electrolyte. A saturated calomel electrode (SCE) reference was used with ferrocene as internal standard: E_f(ferrocene) (CH_2Cl_2) +0.57 V, ΔE_p = 70 mV; (MeCN) +0.42 V, 80 mV. Elemental analyses were carried out by the Microanalytical Service, School of Chemistry, University of Birmingham.

Preparations.—$[Mo(NO)L(Cl)(OMe)]PF_6$. A suspension of $[Mo(NO)LCl_2]PF_6$ (0.21 g, 0.41 mmol) in methanol (20 cm^3) was stirred under reflux for 4 h. The reaction mixture was allowed to cool to room temperature, and then filtered to remove a small amount of a pale green solid which was discarded. A saturated aqueous solution of $NaPF_6$ (5 cm^3) was added to the filtrate. The solution was cooled to 0 °C and, upon evaporation of some of the methanol *in vacuo*, a dark green solid precipitated. This was collected by filtration, washed with cold water, and dried under vacuum at 100 °C for 24 h to yield the product as a dark olive-green powder (0.14 g, 66%) (Found: C, 22.9; H, 4.4; N, 11.8. $C_{10}H_{24}ClF_6MoN_4O_2P$ requires C, 23.6; H, 4.8; N, 11.0%); $\nu_{max}(NO)$ 1670s, $\nu_{max}(PF_6)$ 830s cm^{-1}; δ_H (CD_3COCD_3) 5.50 (3 H, s, OCH_3), 4.0–3.0 (12 H, complex m, 6 CH_2), 3.23, 2.90, and 2.80 (3 H, s; 3 H, s; 3 H, s; 3 × NCH_3).

Complex **2**. A solution of $[Mo(NO)LBr_2]PF_6$ (0.15 g, 0.25 mmol) and 4-amino-2-methyl-4′-ferrocenylazobenzene (0.11 g, 0.28 mmol) was stirred under reflux in dry dichloromethane (20 cm^3) for 3.5 h. The reaction mixture was cooled and filtered in air. The dark red-purple solid was washed with dry dichloromethane (*ca.* 50 cm^3) until the orange filtrate became colourless. The product was dried under vacuum at 100 °C for 24 h to yield a dark red-purple powder (0.17 g, 69%) (Found: C, 38.6; H, 4.2; N, 9.6%; M^+, 853. $C_{32}H_{42}Br_2F_6FeMoN_7OP$ requires C, 38.5; H, 4.2; N, 9.8%; *M*, 852); Λ_M (MeCN) = 112 ohm^{-1} cm^2 mol^{-1}; $\nu_{max}(NH_2)$ 3470w, 3380m, $\nu_{max}(NO)$ 1585s, $\nu_{max}(PF_6)$ 830s cm^{-1}; *m/z* 853 (M^+), 823 (*M* − NO), 772 (*M* − Br), 707 (*M* − L), 692 (*M* − Br_2), 670 [$M - (\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$], 580 [$M - NC_6H_4(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$], 459 ($M - H_2NC_6H_3(CH_3)N{=}NC_6H_4(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$], 428 [$M - H_2NC_6H_3(CH_3)N{=}NC_6H_4(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5) - NO$], and 396 [$H_2NC_6H_3(CH_3)N{=}NC_6H_4(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$]; E_f(Mo) = −1.53 V, ΔE_p = 120 mV; E_f(Fe) = +0.51 V, ΔE_p = 110 mV; μ_{eff} = 3.13.

Discussion

Initially the reactions of $[Mo(NO)LCl_2]^+$ with hydroxy compounds were investigated under conditions similar to those used for the preparation of derivatives of $[Mo(NO)\{HB(3,5\text{-}Me_2C_3HN_2)_3\}Cl_2]$. It was found that the use of triethylamine to consume any HCl liberated resulted in the reduction of the dihalide cation rather than promoting chloride substitution. The reaction with methanol in the absence of base afforded $[Mo(NO)L(Cl)(OMe)]PF_6$ in a reaction analogous to that leading to the known cation $[Mo(NO)L(Cl)(OEt)]^+$. However the reaction with phenol or 4-ferrocenylphenol in CH_2Cl_2 or MeCN failed to produce phenoxide derivatives. Similarly, a reaction with 4-amino-2-methyl-4′-ferrocenylazobenzene in dichloromethane produced a material which did not contain the amine ligand. In a further attempt to prepare the amide complex by MeOH elimination $[Mo(NO)L(Cl)(OMe)]^+$ was treated with 4-amino-2-methyl-4′-ferrocenylazobenzene but again the products were not found to contain the amine ligand.

The bromo-complex $[Mo(NO)LBr_2]^+$ reacted with 4-amino-2-methyl-4′-ferrocenylazobenzene to give a dark red-purple powder which was found to be the paramagnetic 18-electron complex **2** (PF_6 salt), resulting from addition of the neutral ferrocenylamine ligand without any loss of bromide ion. Repeated experiments produced the same product. A room-temperature magnetic moment of μ_{eff} = 3.13 was found in accord with the presence of two unpaired electrons.[13] In an attempt to eliminate HBr from **2** and form the desired amide complex a reaction with the sodium hydride in dry acetonitrile was attempted. However, this failed to produce the required 16-electron complex. The PF_6 salt of complex **2** was tested for powder s.h.g. at 1907 nm but gave no detectable signal.

No reaction could be detected between $[Mo(NO)LBr_2]^+$ and 4-amino-4′-nitroazobenzene or 2-methyl-4-nitroaniline, even after extended periods under reflux in dichloromethane. Aniline, 4-ferrocenyl-2-methylaniline, and triethylamine reacted to produce paramagnetic materials for which evidence of the incorporation of the amine ligand was absent. The results obtained from these experiments suggest that amines which are sufficiently basic simply reduce the dibromide complex without forming an adduct, whereas amines rendered less basic by strongly electron-withdrawing groups do not react at all. In the case of the ferrocenyl derivative it would seem that, rather fortuitously, a situation somewhere in between these two extremes occurs and an 18-electron adduct is obtained.

The reactivity found for $[Mo(NO)LX_2]^+$ may be contrasted with that of the related neutral species $[Mo(NO)\{HB(3,5\text{-}Me_2C_3HN_2)_3\}X_2]$. This readily forms the stable 16-electron complexes $[Mo(NO)\{HB(3,5\text{-}Me_2C_3HN_2)_3\}X(ER)]$ (E = O, S or NH; R = hydrocarbyl) by HX elimination, as well as 17-electron complexes such as $[Mo(NO)\{HB(3,5\text{-}Me_2C_3HN_2)_3\}X(NHC_5H_{10})]$ (X = Cl or I) and $[Mo(NO)\{HB(3,5\text{-}Me_2C_3HN_2)_3\}Cl(NC_5H_5)]$ all of which are six-co-ordinate.[14–17] Two major differences may be identified between $[Mo(NO)\{HB(3,5\text{-}Me_2C_3HN_2)_3\}X_2]$ and $[Mo(NO)LX_2]^+$. The first concerns the steric demands of the ligands in that, while no examples of seven-co-ordination have yet been identified in derivatives of the $[Mo(NO)\{HB(3,5\text{-}Me_2C_3HN_2)_3\}]^{+/2+}$ moiety, seven-co-ordination is possible for $\{Mo(NO)L\}^{3+}$. The second is the difference in the reduction potentials of the two types of compound. In MeCN the reduction potential for $[Mo(NO)LCl_2]PF_6$ is E_f = +0.41 V (ΔE_p = 195 mV) compared to a value of +0.09 V (ΔE_p = 70 mV) for $[Mo(NO)\{HB(3,5\text{-}Me_2C_3HN_2)_3\}Cl_2]$. The values for $[Mo(NO)LBr_2]PF_6$ and $[Mo(NO)\{HB(3,5\text{-}Me_2C_3HN_2)_3\}Br_2]$ in CH_2Cl_2 are respectively E_f = +0.67 V (ΔE_p = 80 mV) and +0.21 V (95 mV). Thus the 16-electron cationic complexes containing L are substantially more powerful oxidants than their neutral counterparts containing $HB(3,5\text{-}Me_2C_3HN_2)_3$. Consequently, while reactions with alcohols give rise to 16-electron alkoxides in both cases, reactions with phenols which are more prone to oxidation can result in the reduction of $[Mo(NO)LX_2]^+$. A similar difficulty appears to exist with arylamine ligands but here adduct formation to give a seven-co-ordinate 16-electron species is also possible. Since the reduction potentials of tungsten complexes containing the $[M(NO)\{HB(3,5\text{-}Me_2C_3HN_2)_3\}]$ (M = Mo or W) moiety are *ca.* 450 mV more cathodic than their molybdenum-containing counterparts[17] it may be possible to develop a chemistry based on the $\{W(NO)L\}^{2+}$ moiety in which the possibility of redox reactions with potential ligands is avoided.

While the objective of obtaining 16-electron cationic molybdenum mononitrosyl complexes has not been realised, the experiments described here do provide further evidence of the special nature of the $HB(3,5\text{-}Me_2C_3HN_2)_3$ ligand in molybdenum mononitrosyl chemistry. Although an extensive derivative chemistry has been developed for the $\{Mo(NO)HB(3,5\text{-}Me_2C_3HN_2)_3\}^{+/2+}$ moiety, attempts to develop a similar chemistry for the related species[18] $[Mo(NO)\{[O{=}P(OEt)_2]_3Co(\eta^5\text{-}C_5H_5)\}]^{2+}$, and now $\{Mo(NO)L\}^{3+}$ have met with far more limited success.

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