The Syntheses and Electrochemistry of Some Molybdenum Mononitrosyl Complexes containing the Tripodal Ligand $[Co(\eta^5-C_5H_5)\{P(=O)(OEt)_2\}_3]^-$

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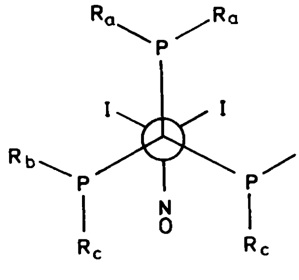
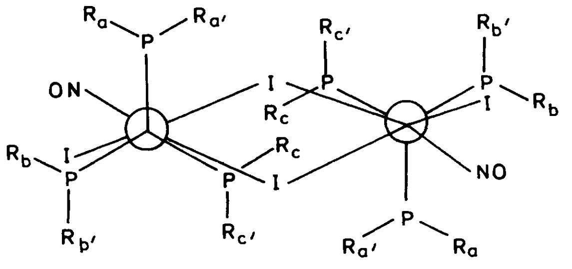
The bimetallic complex $[Mo(NO)(CO)_2L]$ ($L = [Co(\eta^5-C_5H_5)\{P(=O)(OEt)_2\}_3]^-$) may be oxidatively halogenated using iodine to give $[Mo(NO)LI_2]$ which is a monomeric complex containing a 16-electron $\{Mo(NO)\}^4$ moiety. This di-iodide reacts with *p*-toluidine to give $[Mo(NO)LI(NHC_6H_4Me-p)]$ but is decomposed by alcohols or phenols. Reactions with the chelating ligands toluene-3,4-dithiol and 2-aminobenzenethiol afford $[Mo(NO)L\{SC_6H_3(Me)S\}]$ and $[Mo(NO)L(SC_6H_4NH)]$ respectively.

The hydrotris(pyrazol-1-yl)borate ligand, $HB(pz)_3^-$, has been likened to cyclopentadienide $C_5H_5^-$, in so far as both are uninegative, formally six-electron donors which can occupy three facial co-ordination sites on a metal ion.[1] It has been found that complexes containing L tend to be more stable and less reactive than their counterparts containing C_5H_5. In part this may be attributed to the more sterically demanding nature of L, at least in the region of the pyrazole rings. Thus L has a maximum cone angle[2] of *ca.* 180° and its steric properties appear to be more comparable with those of C_5Me_5 than C_5H_5.[3] In the case of the ligand hydrotris(3,5-dimethylpyrazol-1-yl)borate, $HB(Me_2pz)_3$, the 3-methyl substituents project towards the trigonal-prismatic sites on the metal and effectively restrict it to octahedral six-co-ordination.[4] This accounts for the finding that $[\{Mo(NO)(\eta^5-C_5H_5)I_2\}_2]$ exists as a dimer containing seven-co-ordinate 18-electron molybdenum centres, whilst $[Mo(NO)\{HB(Me_2pz)_3\}I_2]$ is monomeric and contains a six-co-ordinate, formally, 16-electron molybdenum centre.[5] However, in addition to these steric differences, C_5H_5, $HB(pz)_3$, and $HB(Me_2pz)_3$ also differ in their electronic properties. Thus in $[Mo(CO)_3(\eta^5-C_5H_5)]$ Curtis *et al.*[2] have shown that a net 0.81 electron is donated to the $\{Mo(CO)_3\}^+$ fragment compared to 1.0 electron in the case of $[Mo(CO)_3\{HB(pz)_3\}]$. Both C_5H_5 and $HB(pz)_3$ were found to be good π donors but poor π acceptors, $HB(pz)_3$ being able to form π bonds to a metal using the σ-donor orbitals of the pyrazolyl nitrogens.[2] These electronic effects are manifest in the carbonyl or nitrosyl stretching frequencies found for related complexes.[6-9]



(*a*)



(*b*)

Figure. Projections down the Co–Mo axis of $[Mo(NO)\{Co(\eta^5-C_5H_5)-[P{=}O(OEt)_2]_3\}I_2]$ omitting the $Co(\eta^5-C_5H_5)$ moiety and with the phosphoryl oxygens lying directly behind the phosphorus atoms shown: (*a*) shows the three non-equivalent ethoxy groups R_a, R_b, and R_c in the monomeric structure; (*b*) shows the six non-equivalent ethoxy groups R_a, $R_{a'}$, R_b, $R_{b'}$, R_c, and $R_{c'}$ in the dimeric structure

The sterically bulky tripodal ligand[10] $[Co(\eta^5-C_5H_5)\{P(=O)(OEt)_2\}_3]^-$, L, is also formally similar to C_5H_5 and, on the basis of infrared data,[11,12] would appear to be a better electron donor than C_5H_5. Although very sterically bulky L is less sterically demanding at the metal surface than $HB(Me_2pz)_3$. The ethoxy substituents in L are, in fact, one atom removed from the metal co-ordination sphere and oriented away from the metal. Furthermore, the absence of any atom in L which corresponds with the pyrazolyl H^3 of $HB(pz)_3$ results in the cone angle for L being substantially less than the 180° reported[2] for $HB(pz)_3$. Overall it might be expected that L would be at least as effective as $HB(Me_2pz)_3$ in stabilising metal centres through electron donation. However, sterically, L would not restrict the metal to octahedral six-co-ordination and, although a highly bulky ligand, it might not be expected to offer the same degree of steric protection to the metal centre as found for $HB(Me_2pz)_3$. Since an extensive derivative chemistry has been developed for the $\{Mo(NO)[HB(Me_2pz)_3]\}^{2+}$ moiety, we were interested to determine whether a similar derivative chemistry might be developed for $\{Mo(NO)[Co(\eta^5-C_5H_5)\{P(O)(OEt)_2\}_3]\}^{2+}$. To this end we have carried out the oxidative iodination of $[Mo(NO)(CO)_2\{Co(\eta^5-C_5H_5)[P(O)(OEt)_2]_3\}]$. A preliminary investigation has also been made into the reactions of the resulting iodide complex with some examples of mono- and bi-dentate ligands.

Experimental

Cobaltocene[13] and $[Co(L)_2]$[14] were prepared by published procedures. The compounds $K[Co(\eta^5-C_5H_5)\{P(O)(OEt)_2\}_3]$ and $[Mo(NO)(CO)_2L]$[11] were prepared by literature procedures with some modifications as described below (L =

$[Co(\eta^5\text{-}C_5H_5)\{P(O)(OEt)_2\}_3]$). Methanol and ethanol were distilled from the respective magnesium alkoxide and stored over 4Å molecular sieves. Diethyl ether and n-hexane were refluxed over sodium wire and subsequently distilled under an atmosphere of nitrogen and stored over 4Å molecular sieves. Dichloromethane was distilled under a nitrogen atmosphere from phosphorus pentoxide and K_2CO_3. Tetrahydrofuran (thf) was purified by distillation from sodium–benzophenone ketyl. Acetonitrile, for electrochemical work, was dried by a procedure involving four steps.[15] All the reactions were routinely carried out under an atmosphere of dry nitrogen. Manipulations involving air-sensitive materials were performed under a nitrogen atmosphere using conventional Schlenk techniques.

Infrared spectra were recorded from KBr discs using a Perkin-Elmer model 297 spectrophotometer. ^1H N.m.r. spectra were recorded using a Bruker WH400 instrument of the S.E.R.C. service at Warwick University. Electrochemical measurements were made at 20 ± 1 °C with a PAR 174 potentiostat and a Philips X–Y recorder. Cyclic voltammetry measurements were carried out using a three-electrode cell which incorporated a saturated calomel electrode (s.c.e.) or a silver wire as the pseudo reference electrode, a platinum-wire auxiliary electrode, and a platinum-bead working electrode. All the electrochemical results were obtained from solutions containing 0.2 mol dm^{-3} $[NBu_4]BF_4$ as supporting electrolyte and the potentials are reported *vs.* s.c.e., but were calibrated using ferrocene as an internal reference couple.

$K[Co(\eta^5\text{-}C_5H_5)\{P(O)(OEt)_2\}_3]$.—A mixture of $[Co_3(\eta^5\text{-}C_5H_5)_2\{P(O)(OEt)_2\}_6]$ (4.00 g, 3.54 mmol) and potassium cyanide (1.61 g, 24.7 mmol) in methanol (50 cm^3) was refluxed for 3 h during which time a yellow adduct was formed. The solvent was then distilled off at room temperature under vacuum to give a yellow powder, which was extracted with water-free diethyl ether (100 cm^3). The extract was separated from $K_3[Co(CN)_6]$ by filtration. The diethyl ether extracts were then combined and evaporated to dryness to give a yellow powder (3.58 g, 88%).

$[Mo(NO)(CO)_2\{Co(\eta^5\text{-}C_5H_5)[P(O)(OEt)_2]_3\}]$.—A mixture of $K[Co(\eta^5\text{-}C_5H_5)\{P(O)(OEt)_2\}_3]$ (2.30 g, 4 mmol) and $Mo(CO)_6$ (1.06 g, 4 mmol) in thf (40 cm^3) was refluxed for 4 h under an atmosphere of nitrogen. The originally yellow solution became deep red during the reaction. The resulting solution was concentrated under vacuum to about half its original volume, and distilled water (20 cm^3) was added. To the aqueous solution, *N*-methyl-*N*-nitroso-*p*-toluenesulphonamide (0.86 g, 4 mmol) was added and the mixture stirred at room temperature overnight under an atmosphere of nitrogen. The colour of the solution changed to yellow and a reddish orange oil formed. The reaction mixture was next concentrated to *ca.* 10 cm^3 under reduced pressure and allowed to stand overnight. Then the orange oil which separated out was isolated by decantation and dried *in vacuo*. The resulting solid was redissolved in chloroform, the solution filtered through Kieselghur, and the filtrate evaporated to dryness. The solid residue was then recrystallised from ethanol and the bright orange crystals which formed were collected by filtration, washed with n-pentane, and dried *in vacuo* (1.80 g; 63% based on $K[Co(\eta^5\text{-}C_5H_5)\{P(O)(OEt)_2\}_3]$).

$[Mo(NO)\{Co(\eta^5\text{-}C_5H_5)[P(O)(OEt)_2]_3\}I_2]$.—Finely divided iodine (0.63 g, 2.5 mmol) was Soxhlet extracted into a solution of $[Mo(NO)(CO)_2\{Co(\eta^5\text{-}C_5H_5)[P(O)(OEt)_2]_3\}]$ (1.79 g, 2.5 mmol) in toluene (150 cm^3) until the extracting solution from the Soxhlet thimble became colourless (*ca.* 18—24 h). The reaction mixture was concentrated and hexane added to effect precipitation of the product. The dark green, almost black, crystalline product (1.81 g, 79%) was collected by filtration, washed with a very small quantity of n-pentane, and dried *in vacuo* (Found: C, 22.9; H, 3.8; I, 27.1; N, 1.8. Calc. for $C_{17}H_{35}CoI_2MoNO_{10}P_3$: C, 22.3; H, 3.8; I, 27.7; N, 1.5%). ν(NO) at 1 685; ν(P=O) at 1 105, 1 085, 1 065 cm^{-1}. Molecular weight in $CHCl_3$ solution 855 (by osmometry; expected 917).

$[Mo(NO)\{Co(\eta^5\text{-}C_5H_5)[P(O)(OEt)_2]_3\}I(NHC_6H_4Me\text{-}p)]$.—A mixture of $[Mo(NO)\{Co(\eta^5\text{-}C_5H_5)[P(O)(OEt)_2]_3\}I_2]$ (0.92 g, 1 mmol), *p*-toluidine (0.11 g, 1 mmol), and anhydrous sodium carbonate (0.5 g) in dichloromethane (50 cm^3) was stirred at room temperature for 4 h, during which the reaction mixture turned reddish brown. The reaction mixture was filtered and the filtrate evaporated to dryness. This crude product was recrystallised from a dichloromethane–hexane–pentane mixture. The brown crystals (0.40 g, 45%) were collected by filtration, washed with n-pentane, and dried *in vacuo* (Found: C, 32.2; H, 4.8; N, 2.8. Calc. for $C_{24}H_{43}CoIMoN_2O_{10}P_3$: C, 32.2; H, 4.9; N, 3.1%). ν(NO) at 1 630; ν(NH) at 3 260; ν(P=O) at 1 105, 1 085 cm^{-1}. Molecular weight in $CHCl_3$ solution 846 (by osmometry; expected 896).

$[Mo(NO)\{Co(\eta^5\text{-}C_5H_5)[P(O)(OEt)_2]_3\}\{SC_6H_3(Me)S\}]$.—To a stirred solution of $[Mo(NO)\{Co(\eta^5\text{-}C_5H_5)[P(O)(OEt)_2]_3\}I_2]$ (0.92 g, 1 mmol) in dichloromethane (100 cm^3), anhydrous sodium carbonate (0.5 g) and toluene-3,4-dithiol (0.16 g, 1 mmol) were added. The resulting mixture was stirred at room temperature for 18 h during which time the solution became deep purple. The reaction mixture was filtered and the solvent removed by evaporation. The crude product was then recrystallised from dichloromethane–hexane to give a purple crystalline solid (0.27 g, 33%) (Found: C, 35.4; H, 5.0; N, 2.0. Calc. for $C_{24}H_{41}CoMoNO_{10}P_3S_2$: C, 35.3; H, 5.1; N, 1.7%). ν(NO) at 1 630; ν(P=O) at 1 115, 1 105, 1 085 cm^{-1}.

$[Mo(NO)\{Co(\eta^5\text{-}C_5H_5)[P(O)(OEt)_2]_3\}(SC_6H_4NH)]$.—A mixture of $[Mo(NO)\{Co(\eta^5\text{-}C_5H_5)[P(O)(OEt)_2]_3\}I_2]$ (0.92 g, 1 mmol), *o*-aminobenzenethiol (0.13 g, 1 mmol), and anhydrous sodium carbonate (0.5 g) was stirred in dichloromethane (50 cm^3) at room temperature for 1.5 h. The deep brown solution was filtered and the solvent removed by evaporation under reduced pressure. The crude product was recrystallised from toluene–hexane to give a dark brown crystalline solid (0.28 g, 36%), which was separated by filtration, washed with n-pentane, and dried *in vacuo* (Found: C, 35.3; H, 5.2; N, 3.6. Calc. for $C_{23}H_{40}CoMoN_2O_{10}P_3S$: C, 35.2; H, 5.1; N, 3.6%). ν(NO) at 1 630; ν(NH) at 3 200; ν(P=O) at 1 120, 1 110, 1 090 cm^{-1}.

Results and Discussion

Synthesis of $[Mo(NO)\{Co(\eta^5\text{-}C_5H_5)[P(O)(OEt)_2]_3\}I_2]$.—The tripodal ligand, $[Co(\eta^5\text{-}C_5H_5)\{P(O)(OEt)_2\}_3]^-$ (L), was obtained as its potassium salt by the reaction of the trinuclear complex, $[Co(L)_2]$ with a six-fold excess of potassium cyanide in refluxing methanol. Evaporation of the solvent at room temperature and extraction of the residue with dry diethyl ether, followed by evaporation of the combined extract gave the compound $K[Co(\eta^5\text{-}C_5H_5)\{P(O)(OEt)_2\}_3]$ (KL) as a bright yellow powder. The method reported[10] in the literature involves the use of sodium cyanide and further extraction with n-pentane. However the quality of KL produced by the above procedure was found to be satisfactory for the preparation of $[Mo(NO)(CO)_2L]$. The previously reported method[11] of preparing $[Mo(NO)(CO)_2L]$ involves refluxing an equimolar mixture of NaL and $Mo(CO)_6$ in acetonitrile, followed by isolation of the air-sensitive product, $Na[Mo(CO)_3L]$, from the reaction mixture. The reaction of $Na[Mo(CO)_3L]$ with *N*-

methyl-*N*-nitroso-*p*-toluenesulphonamide in aqueous thf then gave [Mo(NO)(CO)$_2$L] as an air-stable solid. However, it has been found that there is competition between acetonitrile and L for Mo(CO)$_6$ in the CO displacement reaction. This gives rise to the formation of roughly equal amounts of [Mo(CO)$_3$(CH$_3$CN)$_3$] and [Mo(CO)$_3$L]$^-$.[11] To avoid this difficulty thf was used as a convenient alternative solvent in our synthetic work. The reaction of KL with Mo(CO)$_6$ in thf afforded a deep red air-sensitive solution, presumed to contain [Mo(CO)$_3$L]$^-$. The nitrosylation was carried out using this solution, thereby avoiding any unnecessary isolation of K[Mo(CO)$_3$L]. This approach is similar to that used in the preparations of [Mo(η^5-C$_5$H$_5$)(NO)(CO)$_2$][7] and [Mo(NO)(CO)$_2${HB(Me$_2$pz)$_3$}].[6] Using this procedure the dicarbonyl–nitrosyl complex [Mo(NO)(CO)$_2$L] was obtained in 63% yield as a bright orange crystralline solid which was spectroscopically identical to the material described by Kläui *et al.*[11]

Direct iodination of the nitrosyl–dicarbonyl complex, [Mo(NO)(CO)$_2$L], afforded the dark green di-iodide in an analogous reaction to the conversion of [Mo(η^5-C$_5$H$_5$)(NO)(CO)$_2$] and [Mo(NO)(CO)$_2${HB(Me$_2$pz)$_3$}] to their corresponding di-iodides.[6,7] The new complex [Mo(NO)LI$_2$], (**1**), is a crystalline solid, stable in air for prolonged periods. It is freely soluble in dichloromethane or thf but appears to be unstable in acetonitrile solution.

The i.r. spectrum of (**1**) contained ν(NO) at 1 685 cm^{-1}, a value intermediate between those of 1 670 and 1 700 cm^{-1} found for [{Mo(NO)(η^5-C$_5$H$_5$)I$_2$}$_2$] and [Mo(NO){HB(Me$_2$pz)$_3$}I$_2$], (**2**), respectively. A series of bands were observed in the region 2 870—3 120 cm^{-1} which may be attributed to ν(C–H) from the C$_5$H$_5$ ligand and the ethyl groups in L. The spectrum also contained bands assigned to ν(P=O) in the region 1 065—1 105 cm^{-1}. The mass spectrum of (**1**) did not exhibit a molecular ion, $[M]^+$, but an ion envelope based on m/z = 790 (^{98}Mo, ^{127}I) was observed and may be attributed to $[M - \mathrm{I}]^+$. A strong ion based at m/z = 127 was also observed and attributed to [I]$^+$. The 400-MHz ^{1}H n.m.r. spectrum (Table 1) of (**1**) contained a signal at δ = 5.16 p.p.m. assigned to the C$_5$H$_5$ ligand in L along with signals in the region δ 1.32—1.22 p.p.m. due to the ethoxy methyl groups in L. These signals appeared as three triplets of relative intensity 6:6:6, in accord with a monomeric formulation for (**1**) in CDCl$_3$ solution as illustrated in Figure (*a*). A dimeric formulation containing bridging iodides would give rise to six methyl environments as illustrated in Figure (*b*). The methylene protons of the ethoxy groups constitute AB pairs coupled also to the methyl group, thus they appear as a complex group of overlapping multiplets in the region δ 3.97—4.33 p.p.m. The monomeric formulation was confirmed by an osmometric molecular weight determination in CHCl$_3$ solution. Although large crystals of (**1**) have been obtained, none as yet has proved suitable for an *X*-ray diffraction study to establish the solid-state structure of this di-iodide complex.

Reactions of [Mo(NO){Co(η^5-C$_5$H$_5$)[P(O)(OEt)$_2$]$_3$}I$_2$] *with some monodentate ligands.* In order to investigate whether (**1**) might exhibit a similar halide substitution chemistry to that found for [Mo(NO){HB(Me$_2$pz)$_3$}I$_2$], (**2**), the reactions between (**1**) and several hydroxy compounds were investigated. Methanol did not react readily under ambient conditions but a reaction did occur at reflux in the presence of methoxide ion. Isopropyl alcohol reacted with (**1**) in refluxing CH$_2$Cl$_2$, but phenol only reacted if NaH was added to generate the phenoxide ion. These reactions were all accompanied by a colour change from the green to yellow-brown. In some cases this change only appeared to be complete after 12 h at reflux. The products obtained were oils and neither repeated attempts at recrystallisation from CH$_2$Cl$_2$–hexane mixtures, nor trituration in hexane afforded tractable materials. The i.r.

Table 1. ^{1}H N.m.r. spectral data

Complex	δ[a]	Area[b]	Comment
[Mo(NO)LI$_2$][c]	5.16	5 (s)	η^5-C$_5$H$_5$
	4.33	4 (qnt)	[P(O)(OCH_2CH$_3$)$_2$]$_3$
	4.06	6 (m)	$^3J_{\mathrm{HH}}$ = 7 Hz
	3.97	2 (m)	
	1.32	6 (t)	[P(O)(OCH$_2$CH_3)$_2$]$_3$
	1.25	6 (t)	$^3J_{\mathrm{HH}}$ = 7 Hz
	1.22	6 (t)	
[Mo(NO)LI(NHC$_6$H$_4$-Me-*p*)]	13.09	1 (s)	NHC$_6$H$_4$Me
	7.32	2 (d)	NHC$_6$$H_4$Me
	7.10	2 (d)	AB system $^3J_{\mathrm{HH}}$ = 8 Hz
	5.08	5 (s)	η^5-C$_5$H$_5$
	4.38—4.00	10 (m)	[P(O)(OCH_2CH$_3$)$_2$]$_3$
	3.94	2 (qnt)	$^3J_{\mathrm{HH}}$ = 8 Hz
	2.24	3 (s)	NHC$_6$H$_4$*Me*
	1.205	3 (t)	
	1.215	3 (t)	
	1.285	3 (t)	[P(O)(OCH$_2$CH_3)$_2$]$_3$
	1.305	3 (t)	$^3J_{\mathrm{HH}}$ = 8 Hz
	1.320	3 (t)	
	1.355	3 (t)	
[Mo(NO)L{SC$_6$H$_3$-(Me)S}][c]	7.50	1 (d)	SC$_6$$H_3$(Me)S
	7.46	1 (s br)	$^3J_{\mathrm{HH}}$ = 8 Hz,
	6.92	1 (dd)	$^4J_{\mathrm{HH}}$ = 2 Hz
	4.95	5 (s)	η^5-C$_5$H$_5$
	4.42—4.31	4 (m)	
	4.06—4.00	2 (m)	
	3.99—3.90	2 (m)	[P(O)(OCH_2CH$_3$)$_2$]$_3$
	3.41—3.33	2 (m)	
	3.32—3.24	2 (m)	
	2.33	3 (s)	SC$_6$H$_3$(*Me*)S
	1.41	3 (t)	
	1.40	3 (t)	[P(O)(OCH$_2$CH_3)$_2$]$_3$
	1.22	6 (dt)	$^3J_{\mathrm{HH}}$ = 7 Hz
	0.92	3 (t)	
	0.88	3 (t)	
[Mo(NO)L(SC$_6$H$_4$NH)][c]	11.56	1 (s)	NHC$_6$H$_4$S
	7.83	1 (dd)	NHC$_6$$H_4$S
	7.19	1 (dd)	$^3J_{\mathrm{HH}}$ = 8 Hz
	7.035	1 (dt)	$^4J_{\mathrm{HH}}$ = 1.5 Hz
	6.65	1 (dt)	
	4.88	5 (s)	η^5-C$_5$H$_5$
	4.28—4.00	8 (m)	
	3.48—3.31	1 (m)	[P(O)(OCH_2CH$_3$)$_2$]$_3$
	3.31—3.16	2 (m)	
	2.92—2.83	1 (m)	
	1.33	3 (t)	
	1.30	3 (t)	
	1.25	3 (t)	[P(O)(OCH$_2$CH_3)$_2$]$_3$
	1.22	3 (t)	$^3J_{\mathrm{HH}}$ = 7 Hz
	0.96	3 (t)	
	0.73	3 (t)	

[a] Spectra recorded using a JEOL 270 MHz spectrometer in CDCl$_3$ at ambient temperature. [b] Relative intensity, from integration, s = singlet, d = doublet, t = triplet, qnt = quintet, dd = doublet of doublets, dt = doublet of triplets. [c] Spectra recorded using a Bruker 400 MHz spectrometer in CDCl$_3$ at ambient temperature.

spectra of the crude products contained no characteristic ν(C–H) bands attributable to the ethoxy groups or the C_5H_5 ligand in L. This indicated that the alkoxide ligands were able to displace or destroy the L ligand, thereby leading to the decomposition of the molybdenum complex rather than to a simple halide substitution reaction.

The reaction of (**1**) with *p*-toluidine was also investigated to determine whether aryl amide derivatives of the {Mo(NO)L} moiety could be prepared. The use of NEt_3 to absorb the HI liberated during the reaction to produce an amide complex led to the formation of intractable products. In view of the possibility that NEt_3 might react directly with (**1**) to form an adduct, anhydrous Na_2CO_3 was used as an alternative base. In this case a brown crystalline product, (**3**), could be isolated from the reaction. This material exhibited ν(NO) at 1 630 cm^{-1} in its i.r. spectrum along with other bands attributable to ν(C–H) and ν(P=O). A band at 3 260 cm^{-1} was assigned to ν(N–H) of the amide ligand. The mass spectrum of (**3**) contained a molecular-ion envelope, based at *m*/*z* 896 (^{98}Mo, ^{127}I) along with an ion envelope at *m*/*z* 769 which corresponds with $[M - I]^+$. The 270-MHz ^{1}H n.m.r. spectrum of (**3**) in $CDCl_3$ contained a singlet at δ 5.08 p.p.m. assigned to the C_5H_5 ligand and a singlet at δ 2.24 p.p.m. due to the tolyl methyl group. The aryl protons appeared in the region δ 7.10—7.32 p.p.m. and the ethoxy methylene signals between δ 3.90 and 4.40 p.p.m. The ethoxy methyl resonances appeared as six triplets in the region δ 1.0—1.50 p.p.m. On the basis of these data we formulate (**3**) as the aryl amide derivative $[Mo(NO)\{Co(\eta^5\text{-}C_5H_5)[P(O)(OEt)_2]_3\}I(NHC_6H_4Me\text{-}p)]$. This monomeric formulation was confirmed by a solution molecular weight determination.

Reactions of $[Mo(NO)\{Co(\eta^5\text{-}C_5H_5)[P(O)(OEt)_2]_3\}I_2]$ *with some chelating ligands.* As with the other hydroxylic reagents the reaction between (**1**) and catechol led to decomposition of the molybdenum complex. However, when $HSC_6H_3(Me)SH$ (toluene-3,4-dithiol) was used in the presence of Na_2CO_3 a purple crystalline product, (**4**), was obtained. The i.r. spectrum of this material exhibited ν(NO) at 1 630 cm^{-1} along with other bands attributable to the presence of the $SC_6H_3(Me)S$ and L ligands. The ^{1}H n.m.r. spectrum exhibited a singlet at δ = 4.95 p.p.m. attributable to the C_5H_5 ligand in L, and a singlet at δ = 2.33 p.p.m., attributable to the $SC_6H_3(Me)S$ methyl group. The ethoxy methyl protons of L appeared as six triplets in the region δ = 1.45—0.80 p.p.m., while the methylene protons appeared as a set of overlapping multiplets in the region δ = 4.45—3.20 p.p.m. The aryl protons of the $SC_6H_3(Me)S$ ligand appeared in the region δ = 6.92—7.50 p.p.m. The mass spectrum of (**4**) exhibited a molecular ion $[M]^+$ based at *m*/*z* = 817 (^{98}Mo) as well as an ion envelope at 787 attributed to $[M - (NO)]^+$. The spectral data and elemental analysis of (**4**) were consistent with its formulation as a chelate complex $[Mo(NO)\{Co(\eta^5\text{-}C_5H_5)[P(O)(OEt)_2]_3\}\{SC_6H_3(Me)S\}]$.

The reaction between (**1**) and $HSC_6H_4NH_2$ (*o*-aminobenzenethiol) in the presence of Na_2CO_3 afforded a brown crystalline solid, (**5**), whose i.r. spectrum contained ν(NO) at 1 630 cm^{-1} along with other bands attributable to the presence of the L and SC_6H_4NH ligands. The ^{1}H n.m.r. spectrum of (**5**) contained a singlet at δ = 4.88 p.p.m. attributable to the C_5H_5 ligand in L, and signals in the region δ = 7.83—6.65 p.p.m. attributable to the aryl protons of an SC_6H_4NH ligand. The ethoxy methyl groups in L gave rise to six triplets in the region δ = 0.73—1.33 p.p.m. while the methylene protons appeared as a group of multiplets in the region δ = 2.80—4.30 p.p.m. A broad resonance at δ = 11.56 was assigned to the NH proton of the SC_6H_4NH ligand. The mass spectrum of (**5**) contained an ion envelope based at *m*/*z* = 786 (^{98}Mo) attributable to the molecular ion, $[M]^+$, along with ions corresponding to $[M - (NO)]^+$ and $[M - (NC_6H_4S)]^+$. The data, along with the elemental analysis results are in accord with the formulation of (**5**) as $[Mo(NO)L(SC_6H_4NH)]$. The reactions of (**1**) with 1,2-diaminobenzene (H_2dab) and 2-mercaptopyrimidine were also investigated but in these cases pure products could not be isolated.

Table 2. Electrochemical data

Complex	Solvent	$E_f(V)^a$	$\Delta E_p(mV)^a$	*n*
$[Mo(NO)LI_2]$	CH_2Cl_2	−0.05 (+0.28)	110	1^b
	MeCN	-0.09^c		
	thf	−0.135	210	
$[Mo(NO)LI(NHC_6H_4\text{-}Me\text{-}p)]$	CH_2Cl_2	-1.18^c (−0.84)		1.2^d
		-1.62^c		
$[Mo(NO)L\{SC_6H_3(Me)S\}]$	CH_2Cl_2	−0.81 (−0.35)	100	1.0^d
		−1.79	180	

[a] Values are reported relative to s.c.e. at scan rate = 0.2 V s^{-1}, in the respective solvents containing 0.2 mol dm^{-3} $[NBu_4]BF_4$. Under these conditions E_f for ferrocene, used as an internal standard, was found to be 0.58 V in CH_2Cl_2 with ΔE_p = 100 mV. Corresponding values of E_f in MeCN and thf are 0.43 V with ΔE_p = 80 mV and 0.62 V with ΔE_p = 120 mV, respectively. ΔE_p is the separation between cathodic and anodic peak potentials. Values in parentheses are the corresponding figures for the related complexes containing $HB(Me_2pz)_3$ in place of L. [b] Number of electrons involved in the reduction process, determined by coulometry. [c] E_p^c value, as the complex does not show a reversible wave under these conditions. [d] Number of electrons involved in the process, determined by comparison with $[Mo(NO)LI_2]$.

Electrochemical Studies.—The electrochemical properties of the new complexes were investigated by cyclic voltammetry using solutions in CH_2Cl_2. The results obtained are summarised in Table 2. In the case of $[Mo(NO)LI_2]$ a reversible reduction process was observed at −0.05 V. This was shown by coulometry to involve only one electron. The corresponding reduction potential for $[Mo(NO)\{HB(Me_2pz)_3\}I_2]$ in CH_2Cl_2 is +0.28 V[16] and is in accord with the ligand L being a better electron donor than $HB(Me_2pz)_3$, and so giving rise to a more cathodic reduction potential. Cyclic voltammograms of $[Mo(NO)LI_2]$ were also recorded in thf and MeCN. In thf a quasi reversible reduction was observed at −0.135 V and the initial green colour of the solution persisted for 12 h. However, in MeCN an irreversible reduction wave was observed at −0.09 V and the colour of the solution changed from green to yellow-brown within a few minutes. Two oxidation processes appeared at +0.33 and 0.72 V and these could be enhanced by the addition of $[NBu^n_4]I$. It would appear that in MeCN the complex dissociates I^- in a similar manner to $[Mo(NO)\{HB(Me_2pz)_3\}I_2]$,[5] although the complex containing L appears to be somewhat more reactive than its counterpart containing $HB(Me_2pz)_3$. We were unable to detect any reduction process at more cathodic potentials which might be associated with the Co^{II}–Co^{III} couple of the L ligand.

The complex $[Mo(NO)LI(NHC_6H_4Me\text{-}p)]$ exhibited only irreversible electron transfer processes in CH_2Cl_2. Two reduction waves were observed at E_p^c −1.18 and −1.62 V and it is probable that the irreversible character of the first wave is due to I^- dissociation by analogy with $[Mo(NO)\{HB(Me_2pz)_3\}I(NHC_6H_4Me\text{-}p)]$.[17] An anodic scan following the cathodic scan revealed oxidation processes attributable to the presence of I^- in accord with this proposal. It is possible that the second wave is associated with the reduction of the Co^{III} centre in L. However, in view of the irreversible nature of the first wave, the possibility that this process is associated with a further reduction involving the molybdenum amide moiety cannot be ruled out. It is known[5] that solvated species such as $[Mo(NO)\{HB(Me_2pz)_3\}(MeCN)_2]^+$ can undergo further reduction to 18-electron complexes.

In contrast to the irreversible behaviour observed with the complexes containing the iodide ligand, $[Mo(NO)L\{SC_6H_3(Me)S\}]$ exhibited a reversible one-electron reduction at -0.81 V and a further reduction process at -1.79 V. The former process may be attributed to the reduction of the $\{Mo(NO)\}^{3+}$ core by analogy with $[Mo(NO)\{HB(Me_2pz)_3\}(SPh)_2]$ and $[Mo(NO)\{HB(Me_2pz)_3\}\{SC_6H_3(Me)S\}]$ which reduce at -0.64 (MeCN) and -0.35 (CH_2Cl_2) V respectively.[18,19] The second reduction process may be attributed to the reduction of the Co^{III} centre in L. In free L the two-electron reduction of the Co^{III} centre occurs at -1.87 V in CH_2Cl_2.[20] In the case of $[Mo(NO)L\{SC_6H_3(Me)S\}]$ the second reduction was not reversible and the proximity of the base electrolyte breakdown precluded an accurate assessment of the number of electrons involved.

Conclusions

A comparison of the $\nu(NO)$ values observed for $[Mo(NO)LI_2]$, $[Mo(NO)LI(NHC_6H_4Me\text{-}p)]$ and $[Mo(NO)L\{SC_6H_3(Me)S\}]$ with those found for the analogous complexes containing $HB(Me_2pz)_3$ in place of L reveals a general bathochromic shift in the case of the L complexes. This would be in accord with L donating more electronic charge to the formally 16-electron $\{Mo(NO)\}^4$ core than is the case for $HB(Me_2pz)_3$. A similar effect is apparent in the electrochemical results. The reduction potentials of the complexes containing L are significantly more cathodic than those of their counterparts containing $HB(Me_2pz)_3$. In the case of $[Mo(NO)LI_2]$ the cathodic shift is 325 mV while for $[Mo(NO)LI(NHC_6H_4Me\text{-}p)]$ and $[Mo(NO)L\{SC_6H_3(Me)S\}]$ in CH_2Cl_2 they are 340 and 460 mV respectively.[16] A higher electron density on the $\{Mo(NO)\}^4$ core resulting from better electron donation from L would be expected to destabilise the lowest unoccupied molecular orbital (l.u.m.o.) of the molecule with a corresponding cathodic shift in reduction potential.[21]

Sterically L appears less demanding than $HB(Me_2pz)_3$. Although the larger S donor atoms of the $SC_6H_3(Me)S$ ligand allow chelation in $[Mo(NO)\{HB(Me_2pz)_3\}\{SC_6H_3(Me)S\}]$, the analogous complexes containing SC_6H_4NH, dab, or catecholate are not formed. Instead, ligand degradation reactions involving $HB(Me_2pz)_3$ occur presumably because the smaller N or O donor atoms bring the chelating aryl ring into conflict with a 3-Me group on $HB(Me_2pz)_3$. In the case of the $\{Mo(NO)L\}^{2+}$ moiety chelate complexes were obtained with both $SC_6H_3(Me)S$ and SC_6H_4NH, although more complex reactions occurred with H_2dab or catechol. Overall the $\{Mo(NO)L\}$ moiety appears rather less robust than $\{Mo(NO)[HB(Me_2pz)_3]\}$. We have been unable to prepare alkoxide or aryl oxo derivatives of the former although they are well known for the latter. Even the amide derivative $[Mo(NO)LI(NHC_6H_4Me\text{-}p)]$ is far more difficult to prepare and purify than its counterpart containing $HB(Me_2pz)_3$, the L complex being more reactive and less stable.

In the absence of any apparent steric reasons to preclude dimerisation of $[Mo(NO)LI_2]$ to an 18-electron system it is interesting that the compound is monomeric in $CHCl_3$ solutions. It may be that the donor properties of L, being substantially greater than for C_5H_5, stabilise the 16-electron $\{Mo(NO)\}^{3+}$ core to an extent sufficient to prevent dimerisation. A similar effect is found in $[Mo(NO)(\eta^5\text{-}C_5H_5)(SPh)_2]$ where π donation from the sulphur atoms destabilises the l.u.m.o. and opposes dimer formation.[20] Our preliminary studies of the $\{Mo(NO)L\}^{2+}$ system indicate that, while some derivative chemistry is possible, it is more limited than for $\{Mo(NO)[HB(Me_2pz)_3]\}^{2+}$. The improved donor properties of L, compared to $HB(Me_2pz)_3$, appear insufficient to offset the destabilisation resulting from the loss of steric protection in going from $HB(Me_2pz)_3$ to L. Displacement of L from the $\{Mo(NO)\}^{3+}$ core appears far more facile than for $HB(Me_2pz)_3$ and reaction conditions which can promote iodide substitution may also result in displacement of L. This appears to be especially true where oxygen donor ligands are involved.

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