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A Synthetic Approach to Heterobimetallic Complexes where there is no M–M' Bond or Single Atom Bridges, M–X–M' *

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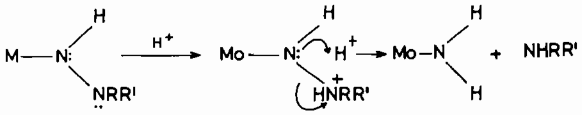
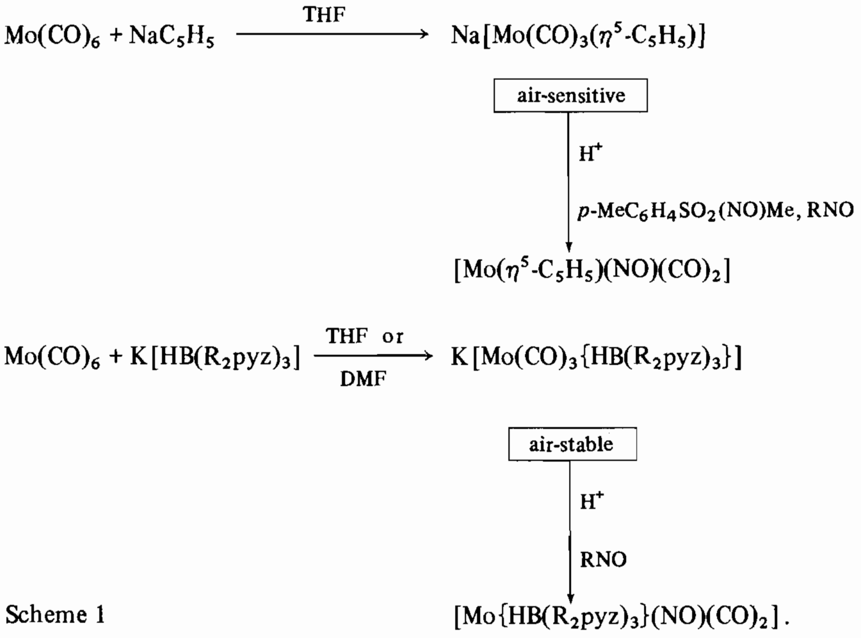
Metal complexes containing tris(pyrazolyl)borato anions, $\{HB(R_2pyz)_3\}^-$ ($R_2pyz = 3,5\text{-}R_2C_3HN_2$ where R = H or Me) are a well-established class of compounds [1, 2]. Trofimenko, the discoverer of the basic ligand system [3], has pointed out that there are strong analogies between the synthesis and some of chemistry of these tris(pyrazolyl)borato complexes and the corresponding η^5-cyclopentadienyl species. For example, the synthesis $[Mo\{HB(Me_2pyz)_3\}(NO)(CO)_2]$ is entirely similar to that of $[Mo(\eta^5\text{-}C_5H_5(NO)(CO)_2]$ (see Scheme 1). However, one advantage of working with the tris(pyrazolyl)borate system is that the intermediates and final products are usually more air-, moisture- and light-stable than their cyclopentadienyl counterparts.

Our particular interest in the tris(pyrazolyl)borate molybdenum system lay in our involvement earlier [4] with the syntheses, structural characterisation, and chemistry of a series of η-cyclopentadienyl hydrazido-(1–) and -(2–) complexes, $[Mo(\eta\text{-}C_5H_5)(NO)I(NHNRR')]$, I, and $[\{Mo(\eta\text{-}C_5H_5)(NO)I\}_2\text{-}NNRR']$, II. We had observed that neither I nor II reacted with hydrohalic acid to release the hydrazine and/or ammonia and amine. This was in direct contrast to the behaviour of certain tertiary phosphine complexes of molybdenum, $[Mo(PR_3)_3(:NNH_2)X_2]$, where ammonia and hydrazine are readily produced after treatment with H^+ [5] (see Scheme 2).



Scheme 2



Scheme 1

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*Synopsis of a lecture given at the EUCHEM CONFERENCE 'The Challenge of Polynuclear Inorganic Compounds', Venice, 28th–30th September, 1981.

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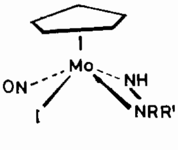
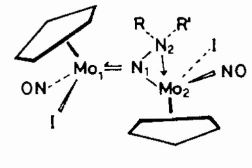
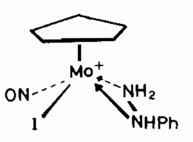
We rationalised our unexpected findings on the basis of the dihapto nature of the hydrazido ligand, particularly as exemplified by I, where addition of acid afforded (reversibly) the stable dihapto *hydrazine* complex III, $[Mo(\eta\text{-}C_5H_5)(NO)I(NH_2HRR')]^+$. We reasoned that the metal atom in III was 'electron-poor', in relation to that in $[Mo(PR_3)_3(NNH_2)X_2]$, and that for this reason, the molybdenum in the cyclopentadienyl species wishes to retain both N atoms of a hydrazine group. Once mono-protonated, as in III, there is no further possibility for addition of H^+ since the remaining electron lone-pairs are used to bind NH_2NRR' to the metal. Consequently no pathway exists to facilitate the break-up of the hydrazine into NH_3 and $NHRR'$.



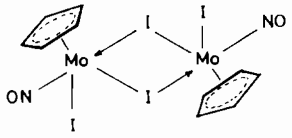
I



II



III



IV

We decided to prepare analogues of these cyclopentadienyl hydrazido species, containing a ligand bulkier than C_5H_5 which would effectively prevent one N atom of the hydrazido(1–) fragment from binding to the metal. If this could be achieved, then a possible route to the acid-assisted decomposition of the hydrazide might be open. Because of Trofimenko's earlier work, we realised that the $HB(3,5\text{-}Me_2C_3HN_2)_3$ ligand, henceforth $\{HB(Me_2pyz)\}$, might fulfil our expectations. Thus we embarked on the synthesis and exploitation of nitrosyl tris(3,5-dimethylpyrazolyl)borato complexes of molybdenum and tungsten.

Preparation of the precursor to all our subsequent work, namely $[Mo\{HB(Me_2pyz)_3\}(NO)I_2]$ is straightforward and is entirely similar to that of $[Mo(\eta\text{-}C_5H_5)(NO)I_2]_2$ [6, 7]. However, a major and most encouraging difference between the $HB(Me_2pyz)_3$ and $\eta\text{-}C_5H_5$ nitrosyl iodo-complexes was our observation that the latter is *dimeric*, having a halide bridged system, IV, the metal atom thereby attaining a formal 18-electron configuration, whereas the former is *monomeric* [7, 8]. The inability of $[Mo\{HB(Me_2pyz)_3\}(NO)I_2]$ to dimerise must lie in the inhibition of iodine-bridge formation by the bulky $HB(Me_2pyz)_3$ ligand. The immediate consequence of this is the metal atom is coordinatively unsaturated (the Mo has a formal 16-e configuration) but it is unable to expand its coordination sphere to 7 or 8 which is more normal for complexes of the type $\{Mo(NO)\}^{3+}$.

In attempting to recrystallise $[Mo\{HB(Me_2pyz)_3\}(NO)I_2]$ from ethanol, we found that the dark brown species was readily converted, in the refluxing alcohol, into an air- and moisture-stable green ethoxide, $[Mo\{HB(Me_2pyz)_3\}(NO)I(OEt)]$. A thorough exploration has been made of the scope of this reaction, and we have prepared a wide range of species $[Mo\{HB(Me_2pyz)_3\}(NO)X(OR)]$, where X = F, Cl, Br or I and R = H, alkyl or CH_2Ph [7, 9]. Related phenoxides, $[Mo\{HB(Me_2pyz)_3\}(NO)X(OC_6H_4R')]$ (R' = H or Me) have also been prepared [10]. Apart from the unusual stability of these complexes towards air and moisture (this is in direct contrast to the usual behaviour of molybdenum(III) and (IV) alkoxides [11]), we found from an X-ray crystal structure determination of $[Mo\{HB(3,5\text{-}Me_2\text{-}4\text{-}ClC_3N_2)_3\}(NO)Cl(OPr^i)]$ (Fig. 1) [7] that the Mo–O bond length (1.86 Å) was unusually short. On the basis of simple covalent radii calculations (making reasonable assumptions about the formal oxidation state of the metal), we would have expected this bond to be longer (*ca.* 2.11 Å), and we explain its contraction in terms of $p(\pi) \rightarrow d(\pi)$ donation from O to Mo. We think that this occurs in order to overcome the 'electron deficiency' at the metal. A consequence of O–Mo bonding is that the Mo–O–C bond angle opens out to 132°. The details of the structure indicated quite clearly that there was steric overcrowding at the metal and that accommodation of a further ligand at the metal would be impossible.

By treatment of $[Mo\{HB(Me_2pyz)_3\}(NO)I(OR)]$ with AgOAc in an alcohol, R'OH, we could obtain pink bis-alkoxides, $[Mo\{HB(Me_2pyz)_3\}(NO)(OR)OR']$. The structures of the complexes with R = R' = Et and Pr^i, and R = Et, R' = Pr^i, have been determined crystallographically [12], the last being a rare example of a kinetically stable mixed alkoxide species. Again the Mo–O bond distances were shorter

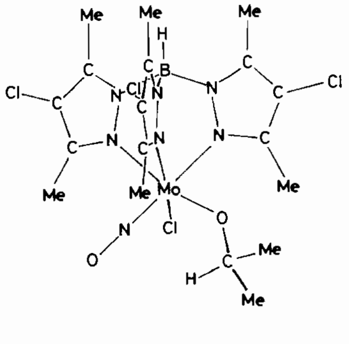


Fig. 1.

than expected (*ca.* 1.90 Å). It was also possible to make brown mono-thiolato species [Mo{HB(Me_2-pyz)$_3$}(NO)I(SR)] (R = alkyl, Ph) but under conditions a little more vigorous than those needed to make the corresponding alkoxides. The dark green bis(thiolates) were obtained by reaction of the diiodide precursor with two mol equivalents of AgOAc followed by addition of the appropriate thiol [13].

The remarkable stability, and relative ease of synthesis, of the monoalkoxide complexes led us to speculate on the possibility of synthesising the isoelectronic monoalkylamides, [Mo{HB(Me_2pyz)$_3$}-(NO)I(NHR)]. Monomeric monoalkylamido species are very rare, partly because of their tendency to oligomerise or polymerise [14], and partly because they can be relatively easily deprotonated giving alkylimido species [15]. However, a few such complexes, derived from bulky primary amines, *e.g.* 1-adamantyl- or t-butyl-amine, [W(=NR)$_2$(NHR)$_2$], *trans*-Mo(NHR)$_2$(OSiMe$_3$)$_4$ [16], are known and probably owe their existence as discrete monomers to steric hindrance.

Reaction of [Mo{HB(Me_2pyz)$_3$}(NO)I_2] with NH_2R afforded [17], immediately and under very mild conditions, the orange monoalkylamido complexes [Mo{HB(Me_2pyz)$_3$}(NO)(NHR)] (R = H, alkyl or CH_2Ph). These species, like their alkoxy analogues, are air- and moisture-stable, and only treatment with acid results in the cleavage of the Mo–N bond. Related red monarylamido species are also relatively easy to prepare.

An X-ray structural examination of [Mo{HB(Me_2-pyz)$_3$}(NO)I(NHR)], R = Et (Fig. 2), *p*-MeC$_6$H$_4$ and *p*-MeOC$_6$H$_4$, established that the Mo–N bond was quite short (1.90–2.00 Å). This situation may be compared with the Mo–N distances in [{Mo(η-C$_5$-H$_5$)(NO)I}$_2$NNMe$_2$], III (R = R′ = Me) [18]. In the cyclopentadienyl species, where the metal atoms are broadly in a similar electronic situation to that in the tris(pyrazolyl)borates, the Mo(2)–N(2) distance is defined as a simple σ bond, where an electron pair is donated from sp^3-hybridised N(2) to the metal. The bond length is 2.13 Å. However, the separation between Mo(1) and N(1) is much shorter, 1.91 Å. In keeping with the electronic requirements of Mo(1) and the coplanarity of the unit Mo(1)N(1)N(2)-Mo(2), which implies sp^2 hybridisation of N(1), there must be $p(\pi) \rightarrow d(\pi)$ donation from N(1) to Mo(1). The short bond distance is a direct reflection of this situation. The same arrangement must occur in [Mo{HB(Me_2pyz)$_3$}(NO)I(NHR)], $p(\pi) \rightarrow d(\pi)$ donation again being necessary to raise the formal outer-valence shell electron configuration of the metal from 16 to 18. From the X-ray data, it was again easy to see that the steric situation at the metal is such that the coordination sphere could not readily expand. Indeed, models indicated that the possibility of preparing dialkylamido species, [Mo{HB(Me_2-pyz)$_3$}(NO)I(NR$_2$)] would be very restricted. In fact we were only able to isolate the unstable red dimethylamide.

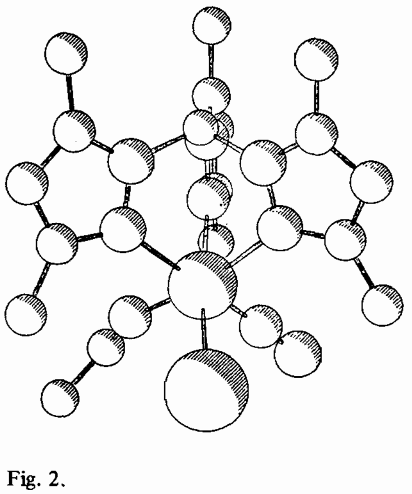


Fig. 2.

At this point, it was quite clear that hydrazido-(1−) complexes, where only one N atom could be accommodated at the metal, would be quite easy to make. Accordingly we prepared the orange or red complexes [Mo{HB(Me_2pyz)$_3$}(NO)I(NHNRR′)] (R = R′ = H, Me or Et; R = H, R′ = Me or Ph; R = Me, R′ = Ph) [19]. In fact, the species containing the group -NHNH$_2$ is probably the only authentic simple hydrazido(1−) species presently known. The properties of these complexes are very similar to those of their monoalkylamido analogues. Thus, treatment with acid effected cleavage of the Mo–N bond:

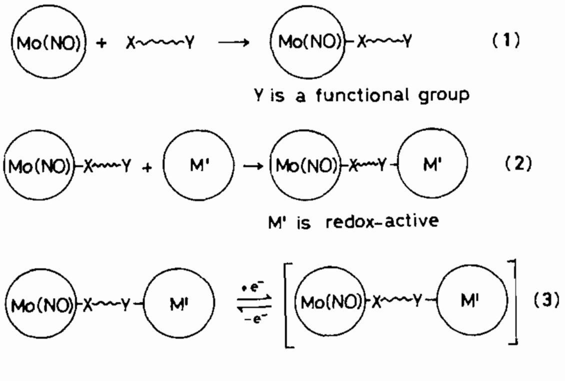
$$[\mathrm{Mo\{HB(Me_2pyz)_3\}(NO)I(NHNRR')}] + 2\mathrm{HX} \rightarrow [\mathrm{Mo\{HB(Me_2pyz)_3\}(NO)IX}] + [\mathrm{RR'NNH_3}]\mathrm{X}$$

This behaviour contrasts with that of Mo(η-C$_5$H$_5$)-(NO)I(NHNRR′), I. While we do not know the mechanism of this reaction, it would appear that the availability of an uncoordinate NRR′ group does not result in N–N bond cleavage, *i.e.* degradation of the hydrazine moiety.

However, the great ease with which the amido and alkoxy complexes we have described could be made opened up other intriguing possibilities. What would happen if the metal in [Mo{HB(Me_2pyz)$_3$}(NO)I_2] had a choice of donor atom in the same ligand? Put more succinctly, would the molybdenum choose N or O if presented with an alkanolamine, NH$_2$(CH$_2$)$_n$-OH, or *p*-aminophenol, *p*-NH$_2$C$_6$H$_4$OH? It should now be remembered that the alkoxides and phenoxides were made under refluxing conditions, whereas the amido species were formed at room temperature. So perhaps appropriate choice of reaction temperature would permit differentiation of the donor atom.

Reaction of $[Mo\{HB(Me_2pyz)_3\}(NO)I_2]$ with alkanolamines or with *p*-substituted anilines, ***at room temperature***, afforded [20, 21] the 'functionalised' complexes, $[Mo\{HB(Me_2pyz)_3\}(NO)I(NHR)]$, where R = $-(CH_2)_nOH$, *p*-C_6H_4OH, *p*-C_6H_5SH and *p*-C_6H_4-NH_2. Thus the N-donor atom was preferentially selected, and these complexes are entirely similar to their more conventional mono-alkyl- and -aryl-amido analogues. It was also possible to prepare 'functionalised' alkoxy and phenoxy species, namely $[Mo\{HB(Me_2pyz)_3\}(NO)I(OR)]$, where R = $-(CH_2)_nOH$, $(CH_2)_nX$ (X = Cl or Br) and *p*-C_6H_4OH. In the complexes involving alkanolamines and aliphatic α,ω-diols we were quite unable to induce chelation, for example, to make $[Mo\{HB(Me_2pyz)_3\}(NO)NH(CH_2)_nO]$, and we suppose that steric hindrance is the cause of this effect.

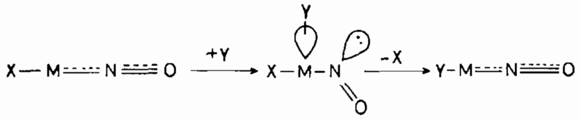
The existence of these stable complexes carrying uncomplexed functional groups, *e.g.* C-OH, C-NH_2, C-SH or C-halide, presented a new and exciting possibility. Would it be possible to bind the molybdenum tris(pyrazolyl)borate group to another metal via these 'free' functional groups? It might then be possible to prepare heterobimetallic complexes where the two metals were ***not*** linked by direct metal–metal bonds, or by single atom bridges (*e.g.* SR, halide, OR, PR_2, CO *etc.*), but where the two metal centres might be quite close to each other. We conceived a plan whereby we could investigate the influence of one metal system upon another, by making one of the partners redox-active and placing useful spectroscopically active ligands on the other. The basic approach is shown in Scheme 3. The interesting question then is, having added an electron to M′, does the Mo(NO) group know about it? In more scientific terms, is a redox reaction at M′ reflected in electronic changes at the Mo atom, as shown by changes in the NO stretching frequency? In a system containing an aromatic bridging group, we might expect a transmission effect, but what about the situation where the bridging group is aliphatic?



Scheme 3

The first problem was obviously the availability of 'functionalised' molybdenum complexes, as shown in Scheme 3, reaction (1). However, we had already achieved this, as described above. The next problem, as outlined in reaction (2), was the formation of the bimetallic species. However, before proceeding to the description of how we succeeded in this venture, we made another surprising but wholly relevant discovery.

Returning briefly to the original syntheses of the alkoxides, thiolates, amides and hydrazides, we began to reflect on the precise mechanism of formation of these complexes from $[Mo\{HB(Me_2pyz)_3\}(NO)I_2]$. Normally, transition metal nitrosyls undergo nucleophilic substitution via an associative process which, it is thought, proceeds via addition of the incoming nucleophile to the coordination sphere of the metal while, simultaneously, the M–N–O bond bends [22]. The effect of bending the metal–nitrosyl bond is to remove two electrons from the outer valence shell of the metal, thereby releasing an orbital to accommodate the incoming nucleophile (Scheme 4). The MNO group then revers to linearity



Scheme 4

at the same time as the leaving group departs. However, in our sterically hindered tris(pyrazolyl)borate complexes, it is a little difficult to visualise an associative process of substituion, even in the transition state (although we admit that our actual knowledge of the transition state is nil!). An alternative mechanism of substitution might be a *dissociative* process as in Scheme 5. If this process occurred, then we should be able to detect I^- in the reaction system. Actually, we found that in all the reactions involving amines and hydrazines two molar equivalents of the nitrogen base were necessary to maximise the yield of the desired complex, one mol to form the compound, and the other to remove liberated HI. However, in the reactions involving alcohols and thiols, observation of I^- in solution would be difficult except by electrochemical (polarographic or cyclic voltammetric) techniques.

Accordingly, we looked first at the cyclic voltammetric behaviour of $[Mo\{HB(Me_2pyz)_3\}(NO)I_2]$. We were astonished to find that, in THF, the complex was itself redox-active, being reduced reversibly in a one-electron step, to the green paramagnetic monoanion $[Mo\{HB(Me_2pyz)_3\}(NO)I_2]^-$, V, (established by cyclic voltammetry, controlled potential electrolysis and coulometry). This species has a characteristic e.s.r. signal (g = 2.206), and we observed that, over a short period of time in strictly

$$\begin{tikzcd}[\mathrm{Mo\{HB(Me_2pyz)_3\}(NO)I_2}] \arrow[r, phantom, "\rightleftharpoons"] & {[\mathrm{Mo\{HB(Me_2pyz)_3\}(NO)I}]^+ \text{ (Solvated)} + \mathrm{I}^-} \arrow[d, "\mathrm{X}^-"] \\ & {[\mathrm{Mo\{HB(Me_2pyz)_3\}(NO)IX}]}\end{tikzcd}$$

Scheme 5

$$\begin{tikzcd}[\mathrm{Mo\{HB(Me_2pyz)_3\}(NO)I_2}] + e^- \arrow[r, phantom, "\rightleftharpoons"] & {[\mathrm{Mo\{HB(Me_2pyz)_3\}(NO)I_2}]^- \text{ (V)}} \arrow[d] \\ {[\mathrm{Mo\{HB(Me_2pyz)_3\}(NO)I}]^+ + e^-} \arrow[r, phantom, "\rightleftharpoons"] & {[\mathrm{Mo\{HB(Me_2pyz)_3\}(NO)I}] \text{ (VI)} + \mathrm{I}^-}\end{tikzcd}$$

Scheme 6

anhydrous conditions, dissociation of I^- occurred, giving a different green paramagnetic but neutral species, $[\mathrm{Mo\{HB(Me_2pyz)_3\}(NO)I}]$ (presumably solvated), VI. This new species could be reversibly oxidised to a monocation, and also had a characteristic e.s.r. signal ($g = 1.998$). The general electron-transfer behaviour can be summarised as in Scheme 6. In strictly anhydrous conditions both V and VI can be detected easily by e.s.r. spectroscopy, but if water, even as minute traces, is present, then the precursor diiodide is *very* rapidly converted into VI. The presence of I^- in the reaction mixture can be clearly demonstrated electrochemically.

The potential for the reduction of the diiodide to V (*ca.* +0.10 V *vs.* SCE) is such that conversion $[\mathrm{Mo\{HB(Me_2pyz)_3\}(NO)I_2}]$ to the monoanion would be expected to occur very easily in the presence of a base, *e.g.* amine or thiol. Thus, we can imagine a mechanism of formation of the amido, hydrazido or thiolato complexes as occuring via a prior electron step (Scheme 7). We can regard QH (RNH_2, $RR'NNH_2$ or RSH) as a reducing agent capable of reducing the diiodide precursor to V which, we know, readily dissociates I^-. The liberated I^- is finally removed from solution as HI($[QH_2]I$) and there is combination of Q with VI to give the final metal-containing product.

$$\begin{array}{lcl}
[\mathrm{Mo\{HB(Me_2pyz)_3\}(NO)I_2}] + \mathrm{QH} & \rightleftharpoons & [\mathrm{Mo\{HB(Me_2pyz)_3\}(NO)I_2}]^- \ \mathrm{V} + [\mathrm{QH}]^+ \\
[\mathrm{Mo\{HB(Me_2pyz)_3\}(NO)I_2}]^- & \rightarrow & [\mathrm{Mo\{HB(Me_2pyz)_3\}(NO)I}] \ \mathrm{VI} + \mathrm{I}^- \\
[\mathrm{QH}]^{+\bullet} & \rightarrow & \mathrm{Q}^\bullet + \mathrm{H}^+ \\
[\mathrm{Mo\{HB(Me_2pyz)_3\}(NO)I}], \mathrm{VI} + \mathrm{Q}^\bullet & \rightarrow & [\mathrm{Mo\{HB(Me_2pyz)_3\}(NO)IQ}] \\
\mathrm{QH} + \mathrm{H}^+ + \mathrm{I}^- & \rightarrow & [\mathrm{QH_2}]\mathrm{I}
\end{array}$$

Scheme 7

However, the reaction of $[\mathrm{Mo\{HB(Me_2pyz)_3\}(NO)I_2}]$ with alcohols is a little more difficult to envisage in terms of a redox reaction. Ethanol cannot be regarded as a particularly powerful reducing agent (the oxidation potential of alcohol to aldehyde is substantially different from that of the molybdenum couple in question). It was observed that water assisted the dissociation of I^- to give VI, perhaps not via a redox process as outlined in Scheme 6, but via protonation of coordinated iodine leading to direct loss of HI. Alcohols could behave similarly, but the detailed mechanism is still an open question and is under further investigation.

It would appear, therefore, that the substitution of I^- in the diiodide precursor occurs via a *dissociative* process, whether or not this is preceded by an electron transfer reaction. However, one of the most significant implications of these observations is that the system $[\mathrm{Mo\{HB(Me_2pyz)_3\}(NO)IX}]$ may be redox-active [24].

This last statement means that the pursuit of our goal, to synthesise heterobimetallic species in which one of the partner metals is redox-active, must be modified slightly. It is apparent, but remains to be thoroughly investigated, that the $\{\mathrm{Mo(NO)}\}$ centre is itself redox-active, so that the other metal (M′) need not be. Ideally, however, M′ should carry a spectroscopically useful ligand (*e.g.* CO or NO). However, cognisance must be taken of the ability of the $\{\mathrm{Mo(NO)}\}$ fragment to undergo redox reactions when attempting to synthesise mixed metal systems.

In devising synthetic routes to heterometallic complexes, we can envisage at least three strategies:

1) synthesis of a 'functionalised' complex $\{Mo(NO)\}-R-OH$, SH or NH_2 and reaction of this species with $[Mo\{HB(Me_2pyz)_3\}(NO)X_2]$ or a related tungsten complex, or indeed any compound having an affinity for an OH, SH or NH_2 group; such a reaction leading to $\{Mo(NO)\}-R-OM'$, $\{Mo(NO)\}-R-SM'$ or $\{Mo(NO)\}-R-NHM'$:

2) oxidative addition of a 'functionalised' complex $\{Mo(NO)\}-R-X$, where X = halide, to low-oxidation state complexes, and formation of a new $M'-C$ bond; such a reaction leading to $\{Mo(NO)\}-R-M'-X$: and

3) nucleophilic displacement of halide from $\{Mo(NO)\}-R-X$ by $[M']^-$, again leading to formation of a new $M'-C$ bond; such a reaction leading to $\{Mo(NO)\}-R-M'$.

Other strategies are obviously possible, but only these three have been studied by us so far.

We have already shown that it is possible to make $[Mo\{HB(Me_2pyz)_3\}(NO)INH(CH_2)_nOH]$ and $[Mo\{HB(Me_2pyz)_3\}(NO)I(NHC_6H_4QH)]$ (Q = O, S or NH). By reaction of these with $[Mo\{HB(Me_2pyz)_3\}(NO)I_2]$ or with $[W\{HB(Me_2pyz)_3\}(NO)Cl_2]$, according to strategy 1, it has been possible to make $[Mo\{HB(Me_2pyz)_3(NO)I\}NH(CH_2)_n\,OMoI(NO)\{HB(Me_2pyz)_3\}]$ and $[Mo\{HB(Me_2pyz)_3\}(NO)I(NHC_6H_4Q)WCl(NO)\{HB(Me_2pyz)_3\}]$ [21].

Formation of the *p*-halo-substituted anilido complex $[Mo\{HB(Me_2pyz)_3\}(NO)I(NHC_6H_4X)]$, especially where X = I, has allowed us to exploit strategy 2. Thus the molybdenum *p*-iodoanilide reacted with $[Pd(PPh_3)_4]$ and $[Pt(PPh_3)_2(C_2H_4)]$ apparently giving the purple $[Mo\{HB(Me_2pyz)_3\}(NO)INHC_6H_4M(PPh_3)_2I]$. However, oxidative addition did not occur with $[Ir(CO)(PPh_3)_2Cl]$, which is not surprising [21].

The same *p*-iodoanilido complex reacted with $LiPPh_2$ or with $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ giving the benzidino complex $[Mo\{HB(Me_2pyz)_3\}(NO)I(p\text{-}NHC_6H_4\text{-})]_2$ and neither $[Mo\{HB(Me_2pyz)_3\}(NO)I(NHC_6H_4PPh_2)$ nor $[Mo\{HB(Me_2pyz)_3\}(NO)INHC_6H_4Fe(CO)_2(\eta\text{-}C_5H_5)]$ [24]. However, reaction with $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$, according to electrochemical evidence [25], apparently afforded $[Mo\{HB(Me_2pyz)_3\}(NO)INHC_6H_4Mo(CO)_3(\eta\text{-}C_5H_5)]$. Thus strategy 3 can only be exploited with caution, and the formation of complexes derived from benzidine raises some interesting questions. For example, is benzidine complex formation a radical process, and how does this relate to the general redox chemistry of $[Mo\{HB(Me_2pyz)_3\}(NO)IX]$?

In conclusion, the general methods of preparing bimetallic complexes based on tris(3,5-dimethylpyrazolyl)borato derivatives of molybdenum and tungsten, whether of homo- or hetero- type, are relatively clear, and need only to be developed to their fullest extent. However, there remains the fascinating question as to the influence of the electrochemical behaviour of the $[M\{HB(ME_2pyz)_3\}(NO)]$ group on the reactivity of the partner metal (M′) system. We have already found that medium or strong reducing agents generally cause total disruption of the $Mo\{HB(Me_2pyz)_3\}(NO)X$ moiety [26]. However, a full understanding of electron transfer reactions in this type of system, and its possible application in certain types of catalysis is the future direction of our research.

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