

## TILDEN LECTURE

### Alkoxy, Amido, Hydrazido, and Related Compounds of Molybdenum and Tungsten

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Late in 1968, I had become very interested in reactions of co-ordinated nitric oxide, particularly in ways to convert NO, *via* transition-metal intermediates perhaps relevant to potential catalytic processes, into organo-nitrogen compounds. Through the encouragement and sponsorship of Monsanto, one of my students, George Kita, began to study the chemistry of  $[\text{Mo}(\text{C}_5\text{H}_5)_2(\text{NO})\text{I}]$ . We picked on this molecule for two reasons: (i) formally, the metal would appear to have a 20-electron configuration, assuming that the rings adopt their normal  $\eta^5$ -bonding mode, and (ii) it was diamagnetic (facilitating n.m.r. spectroscopic studies) and soluble in organic solvents.

In transition-metal nitrosyl chemistry, when one encounters a potentially formal 20-electron configuration, it is usual to find that the  $\text{M}-\text{N}-\text{O}$  bond angle is bent (towards  $120^\circ$ ). In simple terms, this means that the NO group is converted from a 3-electron donor (formally ' $\text{NO}^+$ ' in a linear  $\text{M}-\text{N}-\text{O}$  arrangement, where there is an  $sp$ -hybrid orbital at the N atom) to a 1-electron donor, where the pair of electrons withdrawn from the metal is now located in an  $sp^2$ -hybrid orbital on the N atom (Figure 1). This rather simple formalism, which can, of course, be satisfactorily represented in respectable theoretical terms,<sup>1</sup> has a great advantage in that the predicted location of substantial charge on the NO group, and particularly at the N atom, suggests this atom should be susceptible to electrophilic attack. Over the last few years, the utility of this view has been more than adequately demonstrated;<sup>2</sup> protonation, oxygenation and alkylation of NO being readily achieved *via* systems formally containing ' $\text{NO}^-$ ', *i.e.* having substantially bent  $\text{M}-\text{N}-\text{O}$  bonds.

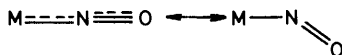


Figure 1

However,  $[\text{Mo}(\text{C}_5\text{H}_5)_2(\text{NO})\text{I}]$  presented several other intriguing possibilities of reactivity. Bruce King, who originally made the compound,<sup>3</sup> had suggested that

<sup>1</sup> R. Hoffmann, M. M.-L. Chen, M. Elian, A. R. Rossi, and D. M. P. Mingos, *Inorg. Chem.*, 1974, **13**, 2666; R. Hoffmann, M. M.-L. Chen, and D. L. Thorn, *ibid.*, 1977, **16**, 503.

<sup>2</sup> J. A. McCleverty, *Chem. Rev.*, 1979, **79**, 53.

<sup>3</sup> R. B. King, *Inorg. Chem.*, 1968, **7**, 90.

the  $^1\text{H}$  n.m.r. spectral equivalence of the cyclopentadienyl protons over the temperature range  $-55$  to  $+33^\circ\text{C}$  could be explained by formulating the complex as  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-C}_5\text{H}_5(\text{NO})\text{I})]$ .<sup>4</sup> In this arrangement, the metal atom would attain the regular 18-electron configuration with the expected linear  $\text{Mo}-\text{N}-\text{O}$  bond system, but, it was suggested, the n.m.r. spectral observations could be explained by rapid rotation of the  $\eta^3$ -ring about the metal-ring axis and interchange of the hapticity between the  $\eta^3$ - and  $\eta^5$ -rings. At this point, even before we began our experimental work, Al Cotton and his group at MIT took an active interest in the problem, being dissatisfied with King's explanation of the n.m.r. behaviour. They examined two complexes crystallographically,  $[\text{Mo}(\text{C}_5\text{H}_5)_2(\text{NO})\text{X}]$ , where  $\text{X} = \text{Me}$  and  $\eta^1\text{-C}_5\text{H}_5$ , discovered that the two rings were structurally equivalent and, on the basis of the rather peculiar  $\text{Mo}-\text{C}$  bond distances, proposed that these rings should be regarded as four-, rather than five-, electron donors.<sup>5</sup> Thus  $[\text{Mo}(\text{C}_5\text{H}_5)_2(\text{NO})\text{X}]$  ( $\text{X} =$  uninegative monohapto-group) would attain the 'magic number' 18 by  $6 + (2 \times 4) + 3 + 1$ . The MIT group further used the concept of tetrahapticity to rationalize the  $^1\text{H}$  n.m.r. spectral behaviour of this and other types of 'anomalous' bis(cyclo-pentadienyl) complexes, e.g.  $[\text{M}(\text{C}_5\text{H}_5)_4]$ , where  $\text{M} = \text{Ti}, \text{Zr},$  or  $\text{Hf}$ .<sup>6</sup>

Our initial foray into the chemistry of the  $[\text{Mo}(\text{C}_5\text{H}_5)_2(\text{NO})\text{X}]$  system was the synthesis, X-ray, and  $^1\text{H}$  n.m.r. spectral characterization of the dithiocarbamates,  $\text{X} = \text{S}_2\text{CNR}_2$  where  $\text{R} = \text{Me}$  or  $\text{Et}$ . The results of our work are described in detail elsewhere,<sup>7</sup> but the important findings were (a) that the ground state of these dithiocarbamates was correctly represented as  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-C}_5\text{H}_5)(\text{NO})(\eta^2\text{-S}_2\text{CNR}_2)]$ , and (b) that the two rings very readily underwent interchange of their hapticity with relative ease ( $\Delta H = 17.6 \pm 0.5$  kcal mol<sup>-1</sup>;  $\Delta S = 1.5 \pm 1.5$  cal K<sup>-1</sup> mol<sup>-1</sup>). The fact that an  $\eta^1$ -cyclopentadienyl ring could be involved in such easy interchange of ring hapticity {as it must be also in  $[\text{M}(\text{C}_5\text{H}_5)_4]$ ,  $\text{M} = \text{Ti}, \text{Zr},$  or  $\text{Hf}$ } induced us to think that, in solution at least, species such as  $[\text{Mo}(\text{C}_5\text{H}_5)_2(\text{NO})\text{I}]$  might contain one monohapto-ring, e.g.  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-C}_5\text{H}_5)(\text{NO})\text{I}(\text{solvent})]$ ; the two rings undergoing rapid electron interchange in  $\eta^1, \eta^2, \eta^3, \eta^4,$  and  $\eta^5$  bonding modes. In the  $\eta^5 : \eta^1$  formulation, the metal formally attains the 18-electron configuration, assuming that one solvent molecule functions as a 2-electron donor by binding to the complex. Interestingly, Hans Brintzinger, Gottfried Huttner, and their co-workers showed that  $[\text{W}(\text{C}_5\text{H}_5)_2(\text{CO})_2]$ , which is isoelectronic with  $[\text{Mo}(\text{C}_5\text{H}_5)_2(\text{NO})\text{X}]$ , existed as  $[\text{W}(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-C}_5\text{H}_5)(\text{CO})_2]$  in the solid state.<sup>8</sup> Thus, there are now examples of cyclopentadienyl rings attached to metals in all bonding modes from  $\eta^1$  to  $\eta^5$ .

<sup>4</sup> R. B. King, *Inorg. Nucl. Chem. Lett.*, 1969, **5**, 901.

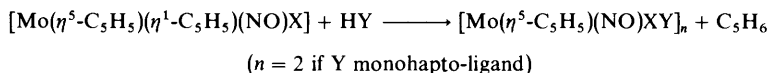
<sup>5</sup> J. L. Calderon, F. A. Cotton, and P. Legzdins, *J. Am. Chem. Soc.*, 1969, **91**, 2528; F. A. Cotton and G. A. Rusholme, *ibid.*, 1972, **94**, 402.

<sup>6</sup> F. A. Cotton, in 'Dynamic Nuclear Magnetic Resonance Spectroscopy', ed. F. A. Cotton and L. M. Jackman, Academic Press, New York, 1975.

<sup>7</sup> M. M. Hunt, W. G. Kita, B. E. Mann, and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 1978, 467.

<sup>8</sup> G. Huttner, H. H. Brintzinger, L. G. Bell, P. Friedrich, V. Bejenke, and D. Neugebauer, *J. Organomet. Chem.*, 1978, **145**, 529.

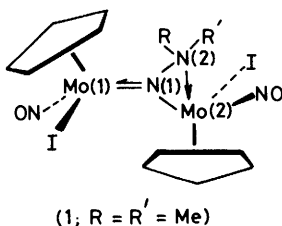
All of this brings us back to the point of departure for George Kita's proposed work. If the NO group was bent and the two rings were normal 5-electron donors, then the N atom should be protonated by acid, *i.e.* the NO would be susceptible to electrophilic attack. If, however,  $[\text{Mo}(\text{C}_5\text{H}_5)_2(\text{NO})\text{X}]$  contained a monohapto-ring in solution, then acid would cleave the Mo—C bond, releasing cyclopentadiene with incorporation of the anion of the acid at the metal *e.g.*



In fact, in view of our work with the dithiocarbamates, and Al Cotton's structural characterization of the species  $[\text{Mo}(\text{C}_5\text{H}_5)_2(\text{NO})\text{X}]$ , X = Me or  $\text{C}_5\text{H}_5$ , we did not seriously expect to find a bent NO group, let alone addition of  $\text{H}^+$  to the N atom.

Our experimental work revealed that cyclopentadiene was lost when acid was added to  $[\text{Mo}(\text{C}_5\text{H}_5)_2(\text{NO})\text{I}]$  and established that, in solution,  $\text{Mo}(\text{C}_5\text{H}_5)_2(\text{NO})\text{I}$  behaved as though it contained both monohapto- and pentahapto-rings.<sup>9</sup>

Thus our original intention to explore the reactivity of the NO had become considerably modified, if not entirely suppressed. During the progress of this work, we decided for reasons none of us were able to satisfactorily explain or rationalize later, that hydrazines might function as suitable 'acids' for attack on  $[\text{Mo}(\text{C}_5\text{H}_5)_2(\text{NO})\text{X}]$ . Using  $\text{NH}_2\text{NHPH}$ , we isolated a yellow microcrystalline material, and with  $\text{NH}_2\text{NMe}_2$  beautiful red crystals were obtained. The latter had a deceptively simple  $^1\text{H}$  n.m.r. spectrum (two  $\text{C}_5\text{H}_5$  and two  $\text{CH}_3$  proton signals), and in our enthusiasm, and under the influence of the growing interest in the reduction of N—N systems to amines and ammonia *via* systems, like the enzyme nitrogenase, containing one, or more probably, two Mo atoms,<sup>10</sup> concluded that we had isolated  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{I}(\mu^2\text{-NMe})_2]$ . We attempted to rush into print, but were saved by a vigilant referee who demanded better evidence for the nature of the so-called  $\mu^2\text{-NMe}$  complex. Ultimately, we persuaded George Sim and David Woodhouse to determine the crystal structure of this material, (1; R = R' = Me). The 'facts' were indeed stranger than our 'fiction', the dimer(1) being asymmetric

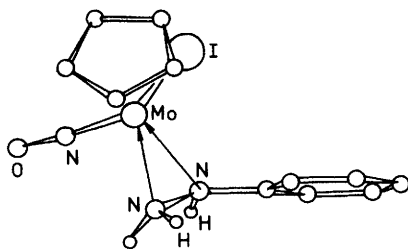


<sup>9</sup> M. M. Hunt, W. G. Kita, and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 1978, 474; M. M. Hunt, W. G. Kita, and J. A. McCleverty, *ibid.*, 1978, 479.

<sup>10</sup> R. C. Burns, R. D. Holsten, and R. W. F. Hardy, *Biochem. Biophys. Res. Commun.*, 1970, **39**, 90; R. W. F. Hardy, R. C. Burns, and G. W. Parshall, *Advances in Chemistry Series*, No. 100, p. 219, American Chemical Society, 1971; E. I. Stiefel, *Proc. Natl. Acad. Sci. USA*, 1973, **70**, 988.

with two apparently different types of Mo atom.<sup>11</sup> This compound is a hydrazido(2-) species, the significant bond lengths and angles being as follows: Mo(1)—N(1) = 1.92 Å, Mo(2)—N(2) = 2.13 Å, Mo(2)—N(1) = 2.05 Å and N(1)—N(2) = 1.40 Å. Mo(2) clearly has an 18-electron configuration by virtue of the three electrons donated by N(1) (one) and N(2) (two), in addition to the other ligands. However, Mo(1) could only attain an 18-electron configuration if N(1) acted as a *three*-electron donor. It could do so by contribution of the  $\sigma$ -electron and by donation of a pair of *p* electrons, the consequences of which being that N(1) would be  $sp^2$ -hybridized. If this was so, then the Mo(1)N(1)—N(2)Mo(2) system would be coplanar, which it was, and the Mo(1)—N(1) distance would be significantly shorter than the Mo(2)—N(2) bond length, which must represent a  $\sigma$ -bond of unit order. This remarkably stable complex was not fluxional—there was no ‘windscreen-wiper’ motion of the NNMe<sub>2</sub> group between Mo(1) and Mo(2), and only in relatively strong acid could it be broken up giving, possibly, [Mo( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(NO)I(NH<sub>x</sub>NMe<sub>2</sub>)]<sup>+</sup>. We were able to make other related species more conveniently by direct reaction of NH<sub>2</sub>NRR' with [Mo( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(NO)I<sub>2</sub>]. Under carefully controlled conditions, we could also produce the hydrazine adducts [Mo( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(NO)I<sub>2</sub>(NH<sub>2</sub>NRR')], but these were obviously highly unstable towards loss of HI.

Because of lack of solubility, the nature of the phenylhydrazido species could not be satisfactorily established. We thought that it might be dimeric, containing  $\eta^2$ -NHNHPh, or that it might be polymeric. However, Doug Frisch was able to protonate it, and isolate nicely crystalline [Mo( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(NO)I(NH<sub>2</sub>NHPh)] [BF<sub>4</sub>]. He, together with my crystallographic colleagues Neil Bailey and Joe



(2)

Walker, established that this salt was monomeric and, remarkably, contained a dihapto hydrazine ligand, (2).<sup>12</sup> We were really pleased with this discovery, as it was the first authentication of a dihapto hydrazine system. Much earlier, Sisler and his colleagues had suggested<sup>13</sup> that AlR<sub>3</sub>(Me<sub>2</sub>NNMe<sub>2</sub>) contained a bidentate hydrazine ligand, but as this claim was made on the basis of relatively low-

<sup>11</sup> W. G. Kita, J. A. McCleverty, B. E. Mann, D. Seddon, G. A. Sim, and D. I. Woodhouse, *J. Chem. Soc., Chem. Commun.*, 1974, 132.

<sup>12</sup> N. A. Bailey, P. D. Frisch, J. A. McCleverty, N. W. Walker, and J. Williams, *J. Chem. Soc., Chem. Commun.*, 1975, 350.

<sup>13</sup> D. F. Clemens, W. S. Brey, and H. H. Sisler, *Inorg. Chem.*, 1963, 2, 1251.

resolution  $^1\text{H}$  n.m.r. spectral studies at one temperature, it could not be substantiated.

These results implied that  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{I}(\text{NHNHPh})]$  contained an  $\eta^2$ -hydrazido(1-) ligand, *i.e.* the grouping shown in Figure 2.

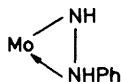
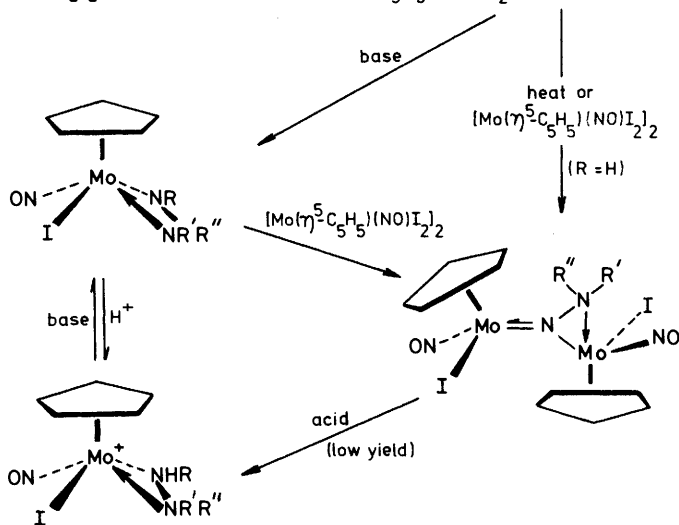
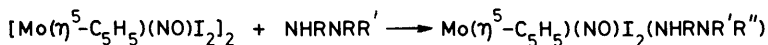


Figure 2

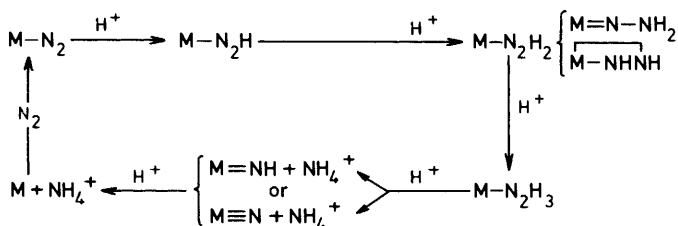
Attempts by an energetic student, Duncan Seddon, to prepare other related species, from alkyl and aryl hydrazines of the type  $\text{NH}_2\text{NHR}$  or  $\text{NH}_2\text{NRR}'$ , led only to the formation of complexes analogous to (1), *viz.*  $[\{\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{I}_2\text{NNRR}'\}]$ . However, by a combination of several peoples' efforts in the group, we synthesized  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{I}_2(\text{NH}_2\text{NMe}_2)]$ ,  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{I}_2(\text{NHMeNHMe}_2)]$  and  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{I}(\text{NMeNMe}_2)]$ , showed that the last was monomeric, that it could be protonated reversibly to give  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{I}(\text{NHMeNMe}_2)]^+$ , and that there was a very close relationship between these three species and  $[\{\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{I}_2\text{NNMe}_2\}]$ , (1). We were then finally able, after nearly seven years of work, to rationalize the rather complex chemistry of this system, and a summary of this is shown in Scheme 1.<sup>14</sup>



Scheme 1

<sup>14</sup> P. D. Frisch, M. M. Hunt, W. G. Kita, J. A. McCleverty, A. E. Rae, D. Seddon, D. Swann, and J. Williams, *J. Chem. Soc., Dalton Trans.*, 1979, 1819.

While we were engaged in this study, major advances were being made in the study of models for the reduction of dinitrogen co-ordinated to transition metals. The group at the ARC Unit of Nitrogen Fixation at the University of Sussex, headed at that time by Professor J. Chatt, had established that  $N_2$ , co-ordinated to low-oxidation state Mo and W tertiary phosphine complexes, could be converted by certain acids into complexes containing hydrazido-(2-) and even, possibly, hydrazido-(1-) ligands. Complexes of the type  $[M(NNH_2)(PMe_2Ph)_3X_2]$ , and  $[M(NNR'R'')(dppe)_2X]^+$  had been prepared, and these species were known to contain linear  $M=N=N$  groups.<sup>15</sup> It was also suggested that  $[WCl_3(N_2H_3)(PMe_2Ph)_2]$  contained the monodentate  $[NHNH_2]$  group,<sup>16</sup> although this compound has now been reformulated as  $[WCl_2H(NNH_2)(PMe_2Ph)_3]Cl$ .<sup>17</sup> Of great significance was the discovery that dinitrogen in Mo and W complexes could be reduced by acid to give ammonia and some hydrazine,<sup>18</sup> and it was initially believed that hydrazido(2-) and (1-) intermediates could be involved.<sup>16,17</sup> Indeed, a scheme was proposed (Scheme 2), whereby successive addition of  $H^+$  to the co-ordinated  $N_2$  led eventually to  $NH_3$  formation.<sup>19</sup> It was felt that these observations might have considerable relevance to the mechanism of reduction of  $N_2$  by the enzyme nitrogenase, where there was strong but circumstantial evidence that the active site for conversion of  $N_2$  to  $NH_3$  involved an Mo atom.<sup>10,20</sup>



Scheme 2

What stimulated our attention was the observation that our hydrazido(1-) species,  $[Mo(\eta^5-C_5H_5)(NO)I(NHNR'R'')]$  reacted with acids to form hydrazines. We could find no evidence for attack by acid on those complexes containing  $[NHNR'R'']^-$  or indeed on the binuclear species  $[[Mo(\eta^5-C_5H_5)(NO)X]_2NNR'R'']$  leading to the formation of either ammonia or amines. The apparent contrast with the results of Chatt, Richards, and their associates, where successive protonation of

<sup>15</sup> V. W. Day, T. A. George, S. D. A. Iske, and S. D. Wagner, *J. Organometal. Chem.*, 1976, **112**, C55; M. Hidai, T. Kodama, M. Sato, M. Harakawa, and Y. Uchida, *Inorg. Chem.*, 1976, **15**, 2694.

<sup>16</sup> J. Chatt, A. J. Pearman, and R. L. Richards, *J. Organomet. Chem.*, 1975, **101**, C45.

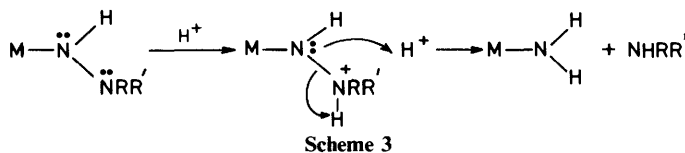
<sup>17</sup> J. Chatt, M. Fakley, P. B. Hitchcock, R. L. Richards, and N. T. Luong-Thi, *J. Chem. Soc., Dalton Trans.*, 1982, 345; T. Takahashi, Y. Mizobe, M. Sato, Y. Uchida, and M. Hidai, *J. Am. Chem. Soc.*, 1980, **102**, 7461.

<sup>18</sup> J. Chatt, G. A. Heath, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1974, 2074; J. Chatt, A. J. Pearman, and R. L. Richards, *Nature*, 1975, **253**, 39; J. Chatt, A. J. Pearman, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1977, 1852.

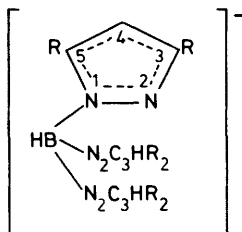
<sup>19</sup> J. Chatt, *J. Organomet. Chem.*, 1975, **100**, 17; J. Chatt and R. L. Richards, *J. Less-Common Met.*, 1977, **54**, 477.

<sup>20</sup> B. E. Smith, 'Proceedings 2nd International Conference, Chemistry and Uses of Molybdenum', Oxford, 1976, p. 237; J. Chatt and R. L. Richards, *ibid.*, p. 242.

monodentate hydrazido species clearly seemed to lead to  $\text{NH}_3$  formation, required some explanation. We concluded that the two sets of observations need not be mutually inconsistent because the electronic situation at the metal atoms in each system was likely to be totally different. Thus, in the nitrosyl complexes, because the metal is relatively 'electron poor', being bound to NO and I which are strongly electron-withdrawing ( $\pi$ ) and electronegative ( $\sigma$ ), respectively, both N atoms of the hydrazido-group are required to relieve the electronic situation at Mo and a very stable three-membered Mo—N—N ring is formed. This has the effect of removing the accessibility of the terminal nitrogen-atom lone-pair for protonation and, apparently, preventing subsequent detachment of that N atom as amine. In the tertiary phosphine complexes, it is accepted that the metal atoms are relatively 'electron rich', and some of the surplus charge is back-donated to the hydrazido-group, thereby making it more susceptible to further protonation and, presumably, to eventual N—N bond cleavage as shown in Scheme 3. What we were saying, in effect, was that the fundamental reason that our complexes did not undergo N—N bond cleavage *via* protonation, whereas the Sussex group's complexes did, was that our species contained the stable three-membered  $\text{Mo}^{\text{I}}\text{—N}^{\text{—}}\text{—N}^{\text{—}}$  ring system, whereas the others had the open-chain configuration  $\text{M}=\text{N}^{\text{—}}\text{—N}^{\text{—}}$ . Therefore, if we could make open-chain hydrazido(1-) species based on the molybdenum nitrosyl species we had already developed, then we, too, might observe protolysis of hydrazido(1-) to amine and  $\text{NH}_3$ .



To prepare compounds as closely similar as possible to our original cyclopentadienyl complexes, but so constructed to *prevent* chelation of the hydrazido(1-) species, did not seem terribly difficult. We contemplated using  $\eta^5\text{-C}_5\text{Me}_5$  systems but, at that time, not having easy access to Mo complexes containing this ligand, and because of the overall cost of making substantial amounts of pentamethylcyclopentadiene, we considered that a reasonable alternative might be to use tris(3,5-dimethylpyrazolyl)borate  $[\text{HB}(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_3]^-$   $\{\text{HB}(\text{Me}_2\text{pyz})^-\}$ , as a ligand, (3).



(3)

Jerry Trofimenko, the inventor and the major developer of pyrazolylborate chemistry,<sup>21</sup> has thoroughly established that there are very strong analogies between the behaviour of metal complexes containing tris-pyrazolylborato anions, and those containing the  $\eta^5$ -cyclopentadienyl ligand. Specifically of relevance to us was Trofimenko's synthesis of  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})(\text{CO})_2]$  from  $\text{Mo}(\text{CO})_6$ ,<sup>22</sup> via a route that entirely parallels Stan Piper's and Geoffrey Wilkinson's original synthesis of  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})(\text{CO})_2]$ .<sup>23</sup>

We know that  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})(\text{CO})_2]$  was relatively easily converted, by reaction with halogen, into  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{X}_2]_2$ .<sup>24</sup> Thus, formation of  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{X}_2]_n$  ( $n = 1$  or  $2$ ), seemed to be relatively straightforward. In the event, only the iodide was easy to obtain, since direct reaction of  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})(\text{CO})_2]$  with chlorine or bromine resulted not only in halogenation of the metal, but also of the 4-position on the pyrazolyl rings, and even the methyl group.<sup>25</sup> Indeed, in the corresponding tungsten chemistry, we actually isolated and characterized the partly ring-brominated species  $[\text{W}\{\text{HB}(\text{Me}_2\text{pyz})_2(3,5\text{-Me}_2\text{-4-BrC}_3\text{H}_2)\}(\text{NO})\text{Br}_2]$ ,<sup>26</sup> and we also have obtained the fully ring-chlorinated  $[\text{Mo}\{\text{HB}(3,5\text{-Me}_2\text{-4-ClC}_3\text{N}_2)_3\}(\text{NO})\text{Cl}_2]$ . Fergus Lalor and his group in Cork claim<sup>27</sup> to be able to make, without apparent difficulties,  $[\text{M}\{\text{HB}(\text{C}_3\text{H}_3\text{N}_2)_3\}(\text{NO})\text{X}_2]$ , where  $\text{M} = \text{Mo}$  or  $\text{W}$  and  $\text{X} = \text{Cl}$ ,  $\text{Br}$ , or  $\text{I}$ , by direct reaction of the appropriate dicarbonyl with halogen, but we were never able to repeat this to our satisfaction.

A most encouraging discovery, made by Duncan Seddon,<sup>25</sup> was that whereas  $[\text{Mo}\{\text{HB}(\text{C}_3\text{H}_3\text{N}_2)_3\}(\text{NO})\text{X}_2]$ ,  $\text{X} = \text{Cl}$  or  $\text{Br}$ , was apparently *dimeric*, the metal atom attaining the 18-electron configuration by halide bridging as in  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{X}_2]_2$ , the related tris-3,5-dimethylpyrazolylborates were certainly *monomeric*, both in the gas phase and in solution. The inability of  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{X}_2]$  to dimerize must lie in the inhibition of halide-bridge formation by the bulky  $\text{HB}(\text{Me}_2\text{pyz})_3$  ligand. The immediate consequence of this is that the metal atom is co-ordinatively unsaturated (the Mo has a formal 16-selection configuration) but it is unable to expand its co-ordination number to 7 or 8 which is more normal for complexes of this type. So our expectations that replacement of  $\text{C}_5\text{H}_5$  by  $\text{HB}(\text{Me}_2\text{pyz})_3$  might lead to hydrazido(1-) molybdenum nitrosyl species where chelation of the  $\text{NHNRR}'$  group was impossible were greatly strengthened.

However, before he embarked on the synthesis of hydrazido-complexes containing  $\text{HB}(\text{Me}_2\text{pyz})_3$ , Duncan Seddon made another discovery. In attempting to recrystallize  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{X}_2]$  from ethanol, a reaction took place

<sup>21</sup> S. Trofimenko, *Acc. Chem. Res.*, 1971, **4**, 17.

<sup>22</sup> S. Trofimenko, *J. Am. Chem. Soc.*, 1969, **91**, 588 and 1967, **89**, 3904.

<sup>23</sup> T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1956, **2**, 28; *ibid.*, 1956, **3**, 104.

<sup>24</sup> J. Bray, W. G. Kita, J. A. McCleverty, and D. Seddon, *Inorg. Synth.*, 1976, **16**, 24.

<sup>25</sup> J. A. McCleverty, D. Seddon, N. A. Bailey, and N. W. Walker, *J. Chem. Soc., Dalton Trans.*, 1976, 898.

<sup>26</sup> J. A. McCleverty, A. E. Rae, I. Wolochowicz, N. A. Bailey, and J. M. A. Smith, *J. Chem. Soc., Dalton Trans.*, 1982, 429.

<sup>27</sup> M. E. Deane and F. J. Lalor, *J. Organomet. Chem.*, 1974, **67**, C19.



resulting in the formation of new complexes. It was hard not to notice that reactions occurred, as both the yellow dichloride and the orange-brown dibromide turned blue, whereas the brown-black di-iodide became green. The new compounds crystallized rapidly and beautifully from the ethanol, and we often speculate what might have remained undiscovered had we, in fact, taken the usual action when molybdenum organometallics and co-ordination compounds turn blue (*i.e.* oxidize).\*

The reaction with alcohols is general, leading to the formation of air- and moisture-stable alkoxides,  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{X}(\text{OR})]^{25,28,29}$  where  $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{or I}$ , and  $\text{R} = \text{Me}, \text{Et}, \text{Pr}^n, \text{Pr}^i, \text{C}_3\text{H}_5, \text{Bu}^n, \text{Bu}^s, \text{CH}_2\text{Ph}, \text{CH}_2\text{CH}_2\text{CH}_2\text{Br}, \text{C}_6\text{H}_{11}, \text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ . Apart from the unusual stability towards air and moisture, which is in direct contrast to the usual behaviour of  $\text{Mo}^{\text{III}}$  and  $\text{Mo}^{\text{IV}}$  alkoxides,<sup>30</sup> Neil Bailey and Joe Walker found from an *X*-ray crystal structure determination of  $[\text{Mo}\{\text{HB}(3,5\text{-Me}_2\text{-4-ClC}_3\text{N}_2)_3\}(\text{NO})\text{Cl}(\text{OPr}^i)]$ , Figure 3<sup>25</sup> that

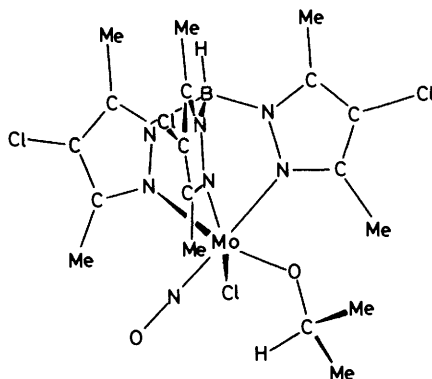


Figure 3

the Mo—O bond length (1.86 Å) was unusually short. On the basis of simple calculations of covalent radii (making reasonable assumptions about the oxidation state of the metal), we would have expected this bond to be about 2.11 Å. We explain its contraction in terms of  $p(\pi) \rightarrow d(\pi)$  donation from O to Mo, *i.e.* that there is significant donation from OR to the metal. We think that this occurs in order to overcome the 'electron deficiency' at the metal: without this donation of electrons from the oxygen atom the Mo formally has a 16-electron configuration. This  $\pi$ -donation is further enhanced by the presence of the strong  $\pi$ -acceptor NO as well as the electronegative halogen, and the  $\text{HB}(\text{Me}_2\text{pyz})_3$  ligand is not an especially

\* Duncan, in fact, claims that he discovered just how nicely  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{Cl}(\text{OEt})]$  crystallized when the ethanol solution containing it hit the water in the laboratory sink.

<sup>28</sup> A. S. Drane and J. A. McCleverty, *Polyhedron*, 1983, 2, 53.

<sup>29</sup> J. A. McCleverty, A. E. Rae, I. Wolochowicz, N. A. Bailey, and J. M. A. Smith, *J. Chem. Soc., Dalton Trans.*, 1982, 951.

<sup>30</sup> D. C. Bradley and M. H. Chisholm, *Acc. Chem. Res.*, 1976, 9, 272; D. C. Bradley, P. D. Gaur, and R. C. Mehrotra, 'Metal Alkoxides', Academic Press, London, New York, San Francisco, 1978.

good donor, either. An additional consequence of Mo=O bonding is that the Mo—O—C bond angle opens out to 132°. Broadly similar observations can be made from the structure of [Mo{HB(Me<sub>2</sub>pyz)<sub>3</sub>}(NO)I(OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br)], where the Mo—O distance is 1.89 Å, and the Mo—O—C bond angle 132°.<sup>31</sup> From a consideration of both structures, the steric overcrowding at the metal caused by the 'endo' methyl groups of the pyrazolyl rings and the virtual impossibility of accommodating a further ligand at the metal centre was quite apparent.

We were initially perplexed by an unusual n.m.r. spectral observation, *viz.* that the chemical shifts of the protons attached to the C atom adjacent to oxygen were unusually low, occurring typically in the region  $\delta = 5.5\text{--}6.5$  p.p.m. Furthermore, the  $\delta(^{13}\text{C})$  of the  $\alpha$ -C atom in [Mo{HB(Me<sub>2</sub>pyz)<sub>3</sub>}(NO)Br(OPr<sup>i</sup>)] occurred at 88.40 p.p.m. (in CDCl<sub>3</sub>), 25 p.p.m. to lower field than free isopropanol. However, in view of the structural information described above, we feel confident that the explanation for this strong deshielding effect on both the <sup>1</sup>H and <sup>13</sup>C resonances lies in the powerful electron-withdrawing nature of the Mo{HB(Me<sub>2</sub>pyz)<sub>3</sub>}(NO)X group, and its underlying co-ordinative unsaturation. This results in a substantial increase in the effective electronegativity of the oxygen atom *vis-à-vis* the alkyl group. Such effects had already been noted, particularly in the <sup>1</sup>H n.m.r. spectra of [WF<sub>5</sub>(OMe)] and *cis*-[WF<sub>4</sub>(OMe)<sub>2</sub>], where the methyl proton signals occurred in the range  $\delta$ -5.3—5.7 p.p.m.<sup>32</sup> We also noted that these  $\alpha$ -protons could not be exchanged with D<sub>2</sub>O, and, so far, we have not been able to carry out any chemistry at the  $\alpha$ -C atom.

By treatment of [Mo{HB(Me<sub>2</sub>pyz)<sub>3</sub>}(NO)I(OR)] with AgOAc in an alcohol, ROH, Liz Rae was able to isolate pink bis-alkoxides, [Mo{HB(Me<sub>2</sub>pyz)<sub>3</sub>}(NO)-(OR)(OR')].<sup>29</sup> We obtained not only the symmetrical species where R = R' = Me, Et, Pr<sup>i</sup>, or Bu<sup>i</sup>, but also the unsymmetrical complexes where R = Et, R' = Pr<sup>i</sup> and R = Pr<sup>i</sup>, R' = Bu<sup>i</sup>. The structure of the complexes where R = R' = Et or Pr<sup>i</sup> and R = Et, R' = Pr<sup>i</sup> were determined crystallographically and again, relatively short Mo—O bond lengths (1.90 Å) and expanded Mo—O—C bond angles (130—133°) were observed.

A post-doctoral associate from Poland, Iwona Wołochowicz, was able to prepare a series of purple monoalkoxide complexes of tungsten, [W{HB(Me<sub>2</sub>pyz)<sub>2</sub>(3,5-Me<sub>2</sub>-4-BrC<sub>3</sub>N<sub>2</sub>)}(NO)Br(OR)], where R = Me, Et, or Pr<sup>i</sup>, as well as the green-brown bis-ethoxide [W{HB(Me<sub>2</sub>pyz)<sub>2</sub>(3,5-Me<sub>2</sub>-4-BrC<sub>3</sub>N<sub>2</sub>)}(NO)(OEt)<sub>2</sub>].<sup>29</sup> More recently, we have succeeded in producing [WHB(Me<sub>2</sub>pyz)<sub>3</sub>-(NO)Cl(OR)], where R = Me, Et, Pr<sup>n</sup>, Pr<sup>i</sup>, Bu<sup>n</sup>, Bu<sup>i</sup>, or CH<sub>2</sub>Ph, from the corresponding tungsten dichloride; these are also purple.

A substantial amount is known about the chemistry of transition-metal alkoxides.<sup>30</sup> The Mo—O bond is susceptible to hydrolysis by water, and will undergo 'insertion' reactions with CO<sub>2</sub> and CS<sub>2</sub>, affording MO<sub>2</sub>COR- and MS<sub>2</sub>COR-containing species. This does not occur in the tris(3,5-dimethylpyrazolyl)borato species, presumably partly because of steric effects.

<sup>31</sup> H. Adams, N. A. Bailey, C. J. Jones, J. A. McCleverty, and S. J. Reynolds, work to be published.

<sup>32</sup> W. McFarlane, A. Noble, and J. M. Winfield, *J. Chem. Soc.*, (A), 1971, 948; F. E. Brinckman, R. B. Johannesen, and L. B. Handy, *J. Fluorine Chem.*, 1972, 1, 493.

However, the Mo—O bond is readily cleaved by acid. In fact, this last property is quite useful in generating  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{X}_2]$  where X = F, Cl, or Br, which are difficult to obtain *via* direct halogenation of the dicarbonyl. Addition of  $\text{HBF}_4$ , HCl, or HBr in appropriate solvents to  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})(\text{OR})_2]$  affords quite good yields of the dihalides.<sup>28</sup> Actually Trofimenko's, reactions of  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})(\text{CO})_2]$  with NOCl or NOBr are probably the most reliable way of producing the dichloride or dibromide in relatively pure form.<sup>22</sup>

The alkoxides proved a relatively easy group of compounds to prepare and characterize. The corresponding aryloxides, because of solubility problems, proved a little more difficult to isolate, but a series of complexes of the type  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{XY}]$ , where X = I, and Y = OPh,  $\text{OC}_6\text{H}_4\text{Me-}p$ , or  $\text{OC}_6\text{H}_4\text{CN-}p$ , which are red-brown, and where X = Y = OPh, which is yellow-brown, have been prepared.<sup>33</sup>

Having spent a considerable time on synthesizing, characterizing, and contemplating the alkoxides, it suddenly dawned on us, in late 1974, that primary amines are isoelectronic with alcohols, and therefore it ought to be possible to prepare monoalkylamido complexes of the type  $[\text{M}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{-X}(\text{NHR})]$ . We were well aware that there were relatively few monoalkylamido complexes known, in contrast to species containing dialkylamido ligands. This is due to the ability of the monoalkylamido species to oligo- or poly-merize, or to undergo proton loss, forming imido species.<sup>34</sup> However, hydrolytically stable  $[\text{TiCl}_2(\text{NHR})_2]$  (R = Me, Et, or  $\text{Pr}^n$ )<sup>35</sup> and  $[\text{W}(=\text{NR})_2(\text{NHR})_2]$  (R = Me, Et, or  $\text{Bu}^n$ )<sup>36</sup> have been reported, and the structure of the bulky 1-adamantyl species *trans*- $[\text{Mo}(\text{NHR})_2(\text{OSiMe}_3)_4]$  has been described.<sup>37</sup>

Reaction of  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{X}_2]$  and its tungsten analogues with primary amines is relatively rapid, and occurs at room temperature.<sup>26</sup> The species  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}(\text{NHR})]$  are orange or orange-pink (R = Me, Et,  $\text{Pr}^n$ ,  $\text{Bu}^n$ ,  $\text{Bu}^i$ ,  $\text{C}_6\text{H}_{11}$ ,  $\text{C}_3\text{H}_5$ , or  $\text{CH}_2\text{Ph}$ ) and, like their alkoxy analogues, are air- and moisture-stable. Only treatment with acid leads to the cleavage of the Mo—N bond, and, unlike binary dialkylamido complexes of Mo and W, they do not undergo 'insertion' reactions with  $\text{CO}_2$  or  $\text{CS}_2$ , giving carbamato or dithiocarbamato complexes.<sup>30</sup>

An interesting amido-derivative,  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}(\text{NH}_2)]$ , obtained by reaction of the di-iodide with ammonia, reacted with acid to give ammonia, and with acetone, in the presence of  $\text{NEt}_3$ , to give  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{-I}(\text{N}=\text{CMe}_2)]$ , as an acetone solvate.<sup>26</sup> Similar products may have been obtained using  $\text{MeCOPh}$  and  $\text{PhCOPh}$ , but we were unable to characterize them. The

<sup>33</sup> J. A. McCleverty, G. Denti, A. S. Drane, N. El Murr, A. E. Rae, S. J. Reynolds, N. A. Bailey, H. Adams, and J. M. A. Smith, *J. Chem. Soc., Dalton Trans.*, 1983, 91.

<sup>34</sup> D. C. Bradley and E. G. Torrible, *Can. J. Chem.*, 1963, **41**, 131; J. N. Armor, *Inorg. Chem.*, 1978, **17**, 203; W. A. Nugent and R. L. Harlow, *J. Chem. Soc., Chem. Commun.*, 1978, 579 and *Inorg. Chem.*, 1979, **18**, 2030; W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev.*, 1980, **31**, 123.

<sup>35</sup> G. W. A. Fowles and F. H. Pollard, *J. Chem. Soc.*, 1953, 2588; R. T. Cowdell and G. W. A. Fowles, *ibid.*, 1960, 2522.

<sup>36</sup> A. A. Kuznetsova, Yu. A. Podozolko, and Yu. A. Buslaev, *Zh. Neorg. Khim.*, 1969, **14**, 751.

<sup>37</sup> W. A. Nugent and R. L. Harlow, *Inorg. Chem.*, 1980, **19**, 777.

ketimido-species could not be formed in the absence of triethylamine, and we think that  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}\{\text{NO}\}\text{I}(\text{NH})]^-$  may be an intermediate in the reaction, the charged  $\text{NH}^-$  group attacking the ketonic function. Metal complexes containing ketimido-groups are quite well-established,<sup>38</sup> and it is possible for the  $\text{N}=\text{CR}_2$  group to act as a monodentate or as a bridging ligand. Unfortunately, we could not obtain a molecular weight for this complex, although we might reasonably expect it to be monomeric. Neither could we obtain suitable crystals for X-ray purposes, and so we cannot establish whether the ketimido-group acts as a 1-electron donor, as, for example, in  $[\text{Rh}(\text{CHMeCH}_2\text{CH}_2\text{NMe})\{\text{N}=\text{C}(\text{CF}_3)_2\}(\text{PPh}_3)_2]$ ,<sup>39</sup> or as a three-electron donor, as in  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{N}=\text{CBu}_2^+)]$ .<sup>40</sup> If it behaved as the latter, then the complex would be electronically equivalent to the known  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}\{\text{NO}\}_2\text{Cl}]$ .<sup>22</sup>

An X-ray structural examination of  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}\{\text{NO}\}\text{I}(\text{NHEt})]$  established<sup>26</sup> that the Mo—N bond is quite short, 1.90—2.00 Å. This situation may be directly compared with that in  $[\{\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{I}\}_2\text{N}_2\text{Me}_2]$ , (1), which contains closely similar molybdenum atoms. In the dimer, Mo(2)—N(2), represents a Mo—N distance (2.3 Å) appropriate to bond order 1. However, the Mo(1)—N(1) bond length is quite similar to that in the ethylamide, and as the former has been described as being appropriate to a  $\text{Mo}\equiv\text{N}$  system, it seems reasonable to regard the NHEt group also as a three-electron donor, *via* a  $\sigma$ -bond and a *p*-electron pair at the nitrogen. Thus the bonding situation, not unexpectedly, is very similar to that in the alkoxides.

We had expected that, on the basis of the structural information now available, and from molecular models based on these, that it would be very difficult to prepare di-alkylamido complexes. This proved to be the case for the iodo-molybdenum system where reaction occurred<sup>26</sup> between the di-iodide precursor and  $\text{NHR}_2$ , ( $\text{R} = \text{Me}$ ,  $\text{Pr}^i$ , or  $\text{C}_6\text{H}_{11}$ ) but we could only isolate the dimethylamide  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}\{\text{NO}\}\text{I}(\text{NMe}_2)]$ . We subsequently observed that the  $\text{NMe}_2$  group was readily replaced by alcohols, phenols, and even monoalkylamines. However, Steve Drane, during his investigation of the chemistry of dichloro- and dibromo-complexes, found that the corresponding chloro- and bromo-dimethylamides were significantly more stable than their iodo-analogue.<sup>28</sup> This may well be a manifestation of reduced steric hindrance when I is replaced by Cl or Br.

Since we had been able to prepare bis-alkoxide complexes, it seemed probable that we could produce the related mixed alkoxide-alkylamido complexes. This was achieved by Liz Rae, who prepared<sup>29</sup> the orange  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}\{\text{NO}\}(\text{OR})(\text{NHR}')] ]$  by treatment of  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}\{\text{NO}\}\text{I}(\text{OR})]$  with  $\text{NH}_2\text{R}'$  either on its own or in the presence of  $\text{AgOAc}$ .

Having reached this point, recognizing the ease with which monoalkylamido complexes could be formed, Liz Rae set out to produce a series of hydrazido(1—)

<sup>38</sup> J. Chatt, R. J. Dossier, F. King, and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1976, 2435; M. Kilner and C. Midcalf, *J. Chem. Soc.*, (A), 1971, 292.

<sup>39</sup> M. J. Doyle, M. F. Lappert, G. M. McLaughlin, and J. McMeeking, *J. Chem. Soc., Dalton Trans.*, 1974, 1494.

<sup>40</sup> H. M. M. Shearer and J. D. Sowerbury, *J. Chem. Soc., Dalton Trans.*, 1973, 2629.

species by treating  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}_2]$  with  $\text{NH}_2\text{NRR}'$ .<sup>41</sup> The orange or red hydrazido(1-) complexes so formed were just as stable as their monoalkylamido analogues and, consistent with our views about the steric situation at the metal, we were unable to produce a hydrazido(1-) complex using  $\text{NHMeNMe}_2$ . Apart from preparing complexes where  $\text{R} = \text{R}' = \text{H}$  or  $\text{Me}$ ,  $\text{R} = \text{H}$ ,  $\text{R}' = \text{Me}$ ,  $\text{Ph}$ , *p*- $\text{MeC}_6\text{H}_4$ , or  $\text{C}_6\text{H}_5$ , or  $\text{R} = \text{Me}$  and  $\text{R}' = \text{Ph}$ , we also obtained complexes where  $\text{R} = \text{H}$  and  $\text{R}' = \text{CSNH}_2$ ,  $\text{CW}_2\text{Me}$ , or  $\text{COPh}$ . We also were able to prepare certain tungsten analogues.

Perhaps the most interesting compounds prepared in this group are  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}(\text{NHNH}_2)]$  and  $[\text{W}\{\text{HB}(\text{Me}_2\text{pyz})_2(3,5\text{-Me}_2\text{-4BrC}_3\text{N}_2)\}(\text{NO})\text{-Br}(\text{NHNH}_2)]$ . We have shown unambiguously by a combination of  $^1\text{H}$  n.m.r. and i.r. spectroscopy that these species are hydrazido(1-) complexes. They also reacted with acetone giving  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}(\text{NHNMe}_2)]$  and  $[\text{W}\{\text{HB}(\text{Me}_2\text{pyz})_2(3,5\text{-Me}_2\text{-4BrC}_3\text{N}_2)\}(\text{NO})\text{Br}(\text{NHNMe}_2)]$ . Such a reaction has been observed with certain hydrazido(2-) species, where, for example, *trans*- $[\text{MX}(=\text{NNH}_2)(\text{diphos})_2]^+$  is converted to *trans*- $[\text{MX}(=\text{N}=\text{N}=\text{CMe}_2)(\text{diphos})_2]^+$ .<sup>42</sup> The structure of two representative hydrazides,  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}(\text{NHNMePh})]$  and its  $\text{NHNMe}_2$  analogue, were determined by Neil Bailey and John Smith. They found, as we expected, that the hydrazido ligand was monodentate, and that there was a relatively short  $\text{Mo}-\text{N}$  bond (1.88 and 1.98 Å, respectively). The  $\text{N}-\text{N}$  distances and the  $\text{Mo}-\text{N}-\text{N}$  bond angles in these two complexes were 1.37 and 1.34 Å, and  $144^\circ$  and  $140^\circ$ , respectively. These data suggest that the hydrazido system may be somewhat delocalized, as in Figure 4.

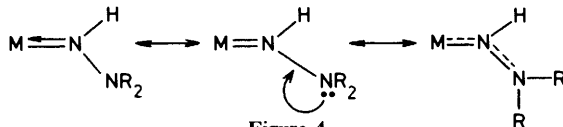


Figure 4

The differences between the two  $\text{Mo}-\text{N}$  distances are a little difficult to explain, although they may be related to high estimated standard deviations, particularly in the complex containing  $\text{NHNMePh}$ .

Those complexes with potentially chelating 'hydrazines', e.g.  $\text{NH}_2\text{NHCOPh}$ , thiosemicarbazide, etc., contained only a monodentate hydrazido(1-) group. Thus, ring systems of the type shown in Figure 5, which are found, for example in  $[\text{MoCl}(\text{N}_2\text{COPh})(\text{NHNCOPh})(\text{PMe}_2\text{Ph})_2]$ ,<sup>43</sup> are not formed.

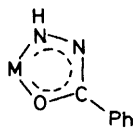


Figure 5

<sup>41</sup> J. A. McCleverty, A. E. Rae, I. Wolochowicz, N. A. Bailey, and J. M. A. Smith, *J. Chem. Soc., Dalton Trans.*, 1983, 71.

<sup>42</sup> M. Hidai, Y. Mizobe, M. Sato, T. Kodama, and Y. Uchida, *J. Am. Chem. Soc.*, 1978, **100**, 5740; P. C. Bevan, J. Chatt, M. Hidai, and G. J. Leigh, *J. Organomet. Chem.*, 1978, **160**, 165.

<sup>43</sup> A. V. Butcher, J. Chatt, J. R. Dilworth, G. J. Leigh, M. B. Hursthouse, S. A. A. Jayaweera, and A. Quick, *J. Chem. Soc., Dalton Trans.*, 1979, 921.

Treatment of these hydrazido(1-) species with acid (usually hydrochloric) caused loss of the hydrazido residue as protonated hydrazine. There was no evidence for ammonia or amine. For example, when  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}(\text{NHNHPh})]$  reacted with HI,  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}_2]$  and  $[\text{PhNHNH}_3]\text{I}$  were isolated. We have no obvious explanation for this behaviour, other than to observe that it is consistent with the chemistry of the corresponding alkoxides and alkyl- or aryl-amides. On the basis of our structural data, and making the wholly reasonable assumption that the strongly electron-withdrawing nature of the metal would reduce the availability of electron density at the  $\alpha$ -nitrogen atom, we would reasonably expect protonation to occur at the unco-ordinated nitrogen. Even when the anion of the acid is non-co-ordinating, as in  $\text{HPF}_6$ , loss of hydrazine occurs.

It is conceivable that in the reaction of the 'electron-rich' hydrazido(2-) species of the Sussex group with acid, hydrazine is formed first, but is decomposed by the metal-containing products of the reaction. This cannot occur in our case, since  $[\text{M}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{X}_2]$  is stable, and would only react with hydrazines to reform the hydrazido(1-) complexes.

Before leaving the subject of hydrazido(1-) complexes, it is appropriate to review briefly what we know of structural types. The best characterized, apart from the Mo complexes described herein,<sup>41</sup> are  $[\text{Ir}(\text{CO})(\text{NHNC}_6\text{H}_4)(\text{PPh}_3)_3][\text{BF}_4]$ ,<sup>44</sup>  $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{NH}_2\text{NAr})][\text{BF}_4]$  ( $\text{Ar} = p\text{-XC}_6\text{H}_4$ ;  $\text{X} = \text{H, Fg, Me, or OMe}$ )<sup>45</sup> and  $[\text{Mo}(\text{NNMe})(\text{NHNMePh})(\text{S}_2\text{CNMe}_2)_2]\text{Cl}$ .<sup>46</sup> Thus we now have four bonding modes for the hydrazido(1-) moiety, A-D in Figure 6.

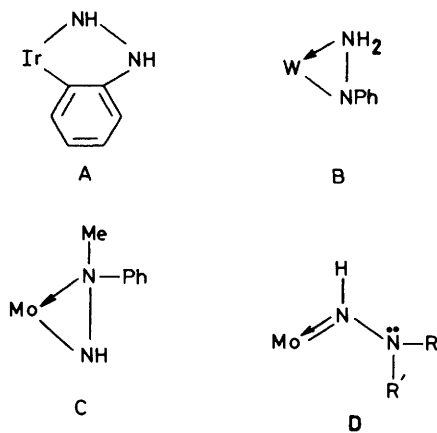


Figure 6

<sup>44</sup> A. B. Gilchrist and D. Sutton, *J. Chem. Soc., Dalton Trans.*, 1977, 677; J. A. Carroll, R. E. Cobbleidick, F. W. B. Einstein, N. Farrell, D. Sutton, and P. L. Vogel, *Inorg. Chem.*, 1977, **16**, 2462.

<sup>45</sup> J. A. Carroll and D. Sutton, *Inorg. Chem.*, 1980, **19**, 3137; M. Cowie and M. D. Gauthier, *ibid.*, 1980, **19**, 3142.

<sup>46</sup> J. Chatt, J. R. Dilworth, P. L. Dahlstrom, and J. Zubietta, *J. Chem. Soc., Chem. Commun.*, 1980, 786.

To conclude the development of the basic chemistry of the tris(3,5-dimethylpyrazolyl)boratomolybdenum and tungsten nitrosyls, we prepared a series of thiolato species. We expected that they should exist, partly by analogy with what had gone before, but mainly because, some years previously Tom James and Duncan Seddon had prepared  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{I}(\text{SR})_2]$  and monomeric  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})(\text{SR})_2]$ .<sup>47</sup> The mono- and di-thiolates proved slightly more difficult to isolate than their alkoxide analogues.<sup>28,48</sup> The complexes  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{X}(\text{SR})]$  and  $[\text{Mo}\{\text{HN}(\text{Me}_2\text{pyz})_3\}(\text{NO})(\text{SR})_2]$  were monomeric, as expected, and our X-ray crystallographic examination of  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}(\text{SC}_6\text{H}_{11})]$  showed that the Mo—S bond length, 2.31 Å, is 0.34 Å shorter than that calculated on simple covalent radii, assuming a Mo—S bond order of unity. Systems formally containing Mo=S bonds exhibit interatomic distances in the range 1.94—2.08 Å.<sup>49</sup> It is difficult to make a meaningful comparison of the Mo—S distance in the cyclohexane thiolate with species containing authentic Mo—S single bonds because of the problem of formulating a precise oxidation state for the metal in this complex. Another difficulty arises because of the possibility of Mo  $\rightarrow$  S( $d_\pi \rightarrow d_\pi$ ) bonding when the metal is in a lower oxidation state (if we assume that these complexes contain 'NO<sup>+</sup>', then we have Mo<sup>II</sup>). Most formal Mo—S single bond distances appear to fall within the range 2.33—2.55 Å, the lowest occurring in  $[\text{Mo}(\text{S}_2\text{C}_2\text{H}_2)_3]$ ,<sup>50</sup> a dithiolene complex which formally contains Mo<sup>VI</sup> (although this oxidation state formalism is not especially meaningful<sup>51</sup>), and the highest in  $[\text{MoCl}(\text{CO})_3(\text{MeSCH}_2\text{CH}_2\text{SMe})(\text{SnCl}_3)]$ , a complex of Mo<sup>II</sup>.<sup>52</sup> In the dithiolene complex, whatever the actual oxidation state of the metal, some S  $\rightarrow$  Mo ( $p_\pi \rightarrow d_\pi$ ) bonding might be expected, and so we believe that the short Mo—S distance in the cyclohexane thiolate is best explained in terms of the normal  $\sigma$ -bond interaction supplemented by donation of  $p$ -electrons from S to the metal to compensate for the co-ordinative unsaturation of the metal and its powerful electron-withdrawing properties.

Earlier, we had prepared the mixed ligand species  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})(\text{OR})(\text{NHR}')]$ . Steve Drane extended the variety of such mixed ligand complexes,<sup>48</sup> by treating  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}(\text{SR})]$  with  $\text{NH}_2\text{R}'$ , to give  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})(\text{SR})\text{NHR}']$ , and with  $\text{AgOAc}$  followed by  $\text{R}'\text{OH}$ , to give  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})(\text{SR})(\text{OR}')]$ . The variety of complexes prepared, together with some of their properties, e.g. colour which is always characteristic, and  $\nu(\text{NO})$  is summarized in Table 1.

In looking at the value of  $\nu(\text{NO})$  for the various types of complex  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{XY}]$ , we can draw certain general, if tentative, con-

<sup>47</sup> T. A. James and J. A. McCleverty, *J. Chem. Soc.*, (A), 1981, 1068; J. A. McCleverty and D. Seddon, *J. Chem. Soc., Dalton Trans.*, 1972, 2588.

<sup>48</sup> J. A. McCleverty, A. S. Drane, N. A. Bailey, and J. M. A. Smith, *J. Chem. Soc., Dalton Trans.*, 1983, 91.

<sup>49</sup> B. Spivack, Z. Dori, and E. I. Stiefel, *Inorg. Nucl. Chem. Lett.*, 1975, 11, 501; G. Bunzey, J. H. Enemark, J. K. Howie, and D. T. Sawyer, *J. Am. Chem. Soc.*, 1979, **99**, 4168.

<sup>50</sup> A. E. Smith, G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *J. Am. Chem. Soc.*, 1965, **87**, 5798.

<sup>51</sup> J. A. McCleverty, *Progr. Inorg. Chem.*, 1968, **10**, 49; G. N. Schrauzer, *Acc. Chem. Res.*, 1969, **2**, 72; R. P. Burns and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 1979, **22**, 303.

<sup>52</sup> R. A. Anderson and F. W. B. Einstein, *Acta Crystallogr., Sect. B.*, 1976, **32**, 966.

Table 1 Tris(pyrazolyl)borates of Mo and W

- 1 = M{HB(Me<sub>2</sub>pyz)<sub>3</sub>}(NO)XY  
 2 = M{HB(py<sub>3</sub>)}(NO)XY  
 3 = Mo{HB(3,5-Me<sub>2</sub>-4XC<sub>3</sub>N<sub>3</sub>)}(NO)XY  
 4 = W{HB(Me<sub>2</sub>pyz)<sub>2</sub>(3,5-Me<sub>2</sub>-4-BrC<sub>3</sub>N<sub>2</sub>)}(NO)XY

Type	M	X	Y	Colour	$\nu(\text{NO})/\text{cm}^{-1}$		Remarks
					KBr	CHCl <sub>3</sub>	
<i>Carbonyl precursors</i>							
1	Mo	CO	CO	orange	1655		
1	W	CO	CO	orange			
2	Mo	CO	CO	orange			
2	W	CO	CO	orange			
<i>Dihalides</i>							
1	Mo	F	F	pale green	1688		
1	Mo	Cl	Cl	yellow	1702	1720	monomeric in CHCl <sub>3</sub>
2	Mo	Cl	Cl	yellow	1710	1727	dimeric by MS
					1700		
1	W	Cl	Cl	bright green			
2	W	Cl	Cl				
1	Mo	Br	Br	orange-brown	1702	1720	monomeric in CHCl <sub>3</sub>
2	Mo	Br	Br	orange	1710	1720	dimeric by MS
					1700		
3	Mo	Br	Br	brown	—	1722	
4	W	Br	Br	fluorescent	1665	—	
				green			
1	Mo	I	I	dark red-brown	1700	1710	monomeric in CHCl <sub>3</sub>
2	Mo	I	I	dark red-brown	1700 s	1716 s	monomeric in MS
					1656 sh	1680 sh	



<i>Alkoxides</i>									
1	Mo	F	OEt	purple	1666	—	insoluble		
1	Mo	Cl	OR	blue	—	1675 av	R = Et, Pr <sup>i</sup>		
3	Mo	Cl	OR	blue	1681 av	1682 av	R = Et, Pr <sup>i</sup>		
1	W	Cl	OR	purple	—	1676 av	R = Et, Pr <sup>i</sup> , C <sub>3</sub> H <sub>5</sub> , Bu <sup>i</sup>		
1	Mo	Br	OR	blue	—	1677	R = Me, Et		
2	Mo	Br	OR	blue	1635 av		R = Me, Et, Pr <sup>i</sup>		
4	W	Br	OR	purple	1675 av	1676 av	R = H, Et, Pr <sup>i</sup> , C <sub>6</sub> H <sub>11</sub> , CH <sub>2</sub> C <sub>2</sub> <sup>—</sup> , CH <sub>2</sub> OH, CH <sub>2</sub> CH <sub>2</sub> Cl, CH <sub>2</sub> CH <sub>2</sub> OMe, CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Br		
1	Mo	I	OR	green	1640 av	1636	R = R' = OH, Me, Et, Pr <sup>i</sup> , Bu <sup>i</sup> , R = Et, R' = OPr <sup>i</sup> , R' = Pr <sup>i</sup> , R' = Bu <sup>i</sup>		
1	Mo	OR	OR'	pink					
4	W	OEt	OEt	yellow-brown	1595				
<i>Aryloxides</i>									
1	Mo	I	OAr	red-brown	1677 av	1682 av	Ar = Ph, <i>p</i> -NCC <sub>6</sub> H <sub>4</sub> , <i>p</i> -MeC <sub>6</sub> H <sub>4</sub>		
1	Mo	OR	OPh	brown	1656 av	1657 av	R = Me, Et		
<i>Alkylamides</i>									
1	Mo	F	NHMe	pale orange	1640	1663 av	R = Me, Et, Bu <sup>n</sup>		
1	Mo	Cl	NHR	orange	1646 av	1667			
1	Mo	Br	NHMe	orange	1654	1668 av	R = H, Me, Et, Pr <sup>n</sup> , Pr <sup>i</sup> , Bu <sup>n</sup> , Bu <sup>i</sup> , CH <sub>2</sub> Ph, C <sub>6</sub> H <sub>11</sub> , C <sub>3</sub> H <sub>5</sub>		
1	Mo	I	NHR	orange-red	1656 av	1623	R = H, Pr <sup>i</sup> , CH <sub>2</sub> Ph		
4	W	Br	NHR	orange	1645	1672			
1	Mo	Cl	NMe <sub>2</sub>	orange	1650	1659			
		Br	NMe <sub>2</sub>	orange	—	1638			
		I	NMe <sub>2</sub>	red	—	1665	(acetone solvate)		
1	Mo	I	N:CMe <sub>2</sub>	orange	—				
<i>Arylamides</i>									
1	Mo	Cl	NHAr	brown	1654 av	1663 av	Ar = Ph, <i>p</i> -MeC <sub>6</sub> H <sub>4</sub>		
1	Mo	I	NHAr	red-brown	1658 av	1666 av	Ar = Ph, naphthyl, <i>p</i> -RC <sub>6</sub> H <sub>4</sub> , where R = Me, Et, MeO, EtO, F, Cl, Br, I, CO <sub>2</sub> Me, NO <sub>2</sub> , CN		

Table 1 (continued)

<i>Mixed alkoxy-amides</i>									
1	Mo	OR	NHR'	orange	1631 av	1631 av	1631 av	R = Me, R' = H, Me, Et; R = Et, R' = Me, Et, Pr <sup>n</sup> , CH <sub>2</sub> Ph, C <sub>6</sub> H <sub>11</sub> ; R = Pr', R' = H, Me, Et, Pr', C <sub>6</sub> H <sub>11</sub>	
1	Mo	OPh	NHMe	red	1650	1650	1657		
<i>Hydrazides</i>									
1	Mo	I	NHNRR'	yellow, orange or red	1637 av	1637 av	1649 av	R = R' = H, Me; R = H, R' = Me, Ph, <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> , C <sub>6</sub> F <sub>5</sub> , CSNH <sub>2</sub> , CO <sub>2</sub> Me, COPh; R = Me, R' = Ph	
4	W	Br	NHNRR'	yellow or red	1615	—	—	R = R' = H, Me; R = H, R' = Ph	
1	Mo	I	NHN=CMe <sub>2</sub>	orange-red	1658	—	—		
4	W	Br	NHN:CMCMe <sub>2</sub>	orange	1630	—	—		
<i>Thiolates</i>									
1	Mo	F	SBu <sup>n</sup>	brown	1655	—	—	insoluble	
1	Mo	Cl	SR	yellow black	1672 av	1683 av	1683 av	R = Bu <sup>n</sup> , C <sub>6</sub> H <sub>11</sub> , CH <sub>2</sub> Ph, Ph	
1	Mo	Br	SBu <sup>n</sup>	olive-green	1665	1682	1682		
1	Mo	I	SR	red-brown	1679 av	1682 av	1682 av	R = Et, Bu <sup>n</sup> , C <sub>6</sub> H <sub>11</sub> , C <sub>16</sub> H <sub>33</sub> , CH <sub>2</sub> Ph, Ph, <i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	
1	Mo	SR	SR	deep green	1667 av	1670 av	1670 av	R = Bu <sup>n</sup> , Ph	
<i>Alkoxy-thiolates</i>									
1	Mo	OR	SR'	brown	1651 av	1657 av	1657 av	R = Me or Et; R' = Bu <sup>n</sup> or Ph	
<i>Amido-thiolates</i>									
1	Mo	NHR	SR'	orange	1635 av	1651 av	1651 av	R = Me, Et, Pr <sup>n</sup> , Bu <sup>n</sup> ; R' = Bu <sup>n</sup> or Ph	
<i>Other complexes</i>									
1	Mo	NCMe	NCMe	green-brown	1652	—	—	As PF <sub>6</sub> <sup>-</sup> cation, paramagnetic ( <i>S</i> = 1), <i>g</i> = 1.982 in MeCN	

clusions. The NO stretching frequencies (average values in KBr discs were used) decrease in the following order: X,Y (average frequency in  $\text{cm}^{-1}$ ,  $\pm 5 \text{ cm}^{-1}$ )—I,SR (1679) > I,OR (1675) > SR,SR (1667) > I,NHR (1656) > SR,OR (1651) > OR,OR (1646) > SR,NHR (1635) > OR,NHR (1632). While these averaged data are of necessity rather crude, they nevertheless reveal a trend which is broadly consistent with the donor capacities of the various donor atoms in X and Y. Thus, in general, the SR groups are less powerful donors than the corresponding alkoxy- and amido-groups, while NHR is the most powerful donor of all the groups involved. We consider it unlikely that the thiolato-groups function as significant  $\pi$ -acceptors, since  $\nu(\text{NO})$  is substantially lower than that when X = Y = halogen, where the halogen groups are, of course, electron-withdrawing,  $\nu(\text{NO})$  occurring above  $1700 \text{ cm}^{-1}$ .

In all of the complexes, the  $^1\text{H}$  n.m.r. spectra show a common feature, which was already noted in the description of the alkoxides. This is that the chemical shifts of the protons attached to the  $\alpha$ -C atom of the donor group resonate at lower fields than would be normally expected. It must be reiterated that this effect is most probably due to the powerfully electron-withdrawing influence of the metal nitrosyl{tris(pyrazolyl)borato} group.

Having reached this point we began to reflect on the mechanism whereby these complexes might be formed. In transition-metal nitrosyl chemistry, ligand substitution normally occurs *via* an associative process.<sup>53</sup> This proceeds *via* addition of the incoming nucleophile to the inner co-ordination shell of the metal while, simultaneously, the M—N—O bond angle bends (Figure 7). The effect of bending

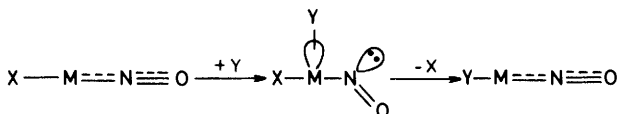
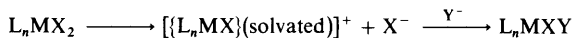


Figure 7

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. The M—N—O group then reverts to linearity at the same time as the leaving group is expelled. However, in these highly sterically hindered tris(3,5-dimethylpyrazolyl)borates, it is a little difficult to envisage an associative process of substitution, even in the transition state. One has to admit, however, that our knowledge of transition states is virtually nil, but an argument has to be presented with some basic assumptions! So if association is unlikely, then is a dissociative process likely? Here, a halide ion would be expelled prior to accommodation of the incoming nucleophile (Figure 8). Even in this process, however, one might reasonably assume that the solvated intermediate would be sterically hindered also. However, the extent of the hindrance might be lower than that in the dihalo precursor. Our initial problem was to discover whether  $\text{X}^-$  was readily liberated

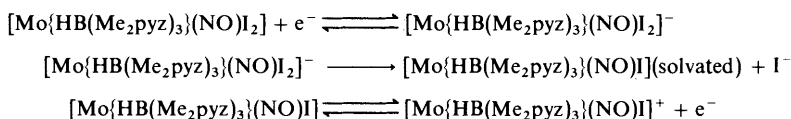
<sup>53</sup> F. Basolo and R. G. Pearson, 'Mechanism of Inorganic Reactions', 2nd. Edition, Wiley, New York, 1967, 571; M. L. Tobe, 'Inorganic Reaction Mechanisms', Nelson, London, 1972, 40 and 153.

from  $[M\{HB(Me_2pyz)_3\}(NO)X_2]$  in various solvents. Nabil El Murr suggested that the easiest way to establish this would be to look for  $I^-$  electrochemically in solutions containing  $[Mo\{HB(Me_2pyz)\}(NO)I_2]$ . This he did, by a combination of polarography, cyclic voltammetry, and coulometry.



**Figure 8**

Nabil's results were astonishing.<sup>54</sup> He found that, in THF, the molybdenum di-iodide was itself redox-active being reduced, in a reversible one-electron step, to a green, paramagnetic mono-anion,  $[Mo\{HB(Me_2pyz)_3\}(NO)I_2]^-$ . This species has a characteristic e.s.r. signal ( $g = 2.206$ ), and he observed that, over a short period of time in strictly anhydrous conditions, dissociation of  $I^-$  occurred, giving a different green, paramagnetic, but neutral species,  $[Mo\{HB(Me_2pyz)_3\}(NO)I]$ , presumably solvated. This new species could be reversibly oxidized to a mono-cation, and also had a characteristic e.s.r. signal ( $g = 1.998$ ). In strictly anhydrous conditions both e.s.r. signals can be detected in the same solution, but if traces of water are present, then the precursor di-iodide is very rapidly converted into  $[Mo\{HB(Me_2pyz)_3\}(NO)I]$ . The presence of  $I^-$  in the reaction mixture can be clearly demonstrated electrochemically. The overall process is shown in Scheme 4. More recent electrochemical studies of  $[M\{HB(Me_2pyz)_3\}(NO)X_2]$ , where  $M = Mo$  and  $X = Cl$  or  $I$ , and  $M = W$ ,  $X = Cl$ , have been carried out in acetonitrile and THF by Sarah Reynolds and Bryan Neaves.<sup>55</sup> They have found that whereas the di-iodide is very unstable in acetonitrile, both dichlorides reduce reversibly and there is no noticeable  $Cl^-$  loss. The same is true in THF, and the overall reduction potentials are summarized in Table 2. It should be noted that there is a pronounced metal and halide influence on the values of  $E_{1/2}$ , and we will return to this point later.



**Scheme 4**

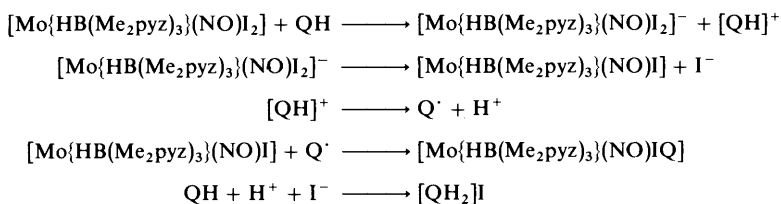
**Table 2**

$M\{HB(Me_2pyz)_3\}(NO)X_2$	$E_{1/2}$		$\Delta E$		$n$	
	MeCN	THF	MeCN	THF	MeCN	THF
$M = Mo; X = Cl$	+0.09	+0.09	70	90	1.0	—
$M = Mo; X = I$	—	+0.22	—	120	—	—
$M = W; X = Cl$	-0.42	-0.46	80	200	1.0	—

<sup>54</sup> J. A. McCleverty and N. El Murr, *J. Chem. Soc., Chem. Comm.*, 1981, 960.

<sup>55</sup> G. Denti, C. J. Jones, J. A. McCleverty, B. D. Neaves, and S. J. Reynolds, *J. Chem. Soc., Chem. Commun.*, 1983, 474.

However, in the case of the molybdenum di-iodide, the value of the reduction potential is such that we would expect conversion into the monoanionic species  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}_2]^-$  to occur very readily in the presence of a base, *e.g.* amine or thiol. Thus, we could imagine a mechanism of formation of the amido, hydrazido, or thiolato complexes as occurring *via* an initial electron-transfer step (Scheme 5). We can regard QH ( $\text{RNH}_2$ ,  $\text{RR}'\text{NNH}_2$ , or  $\text{RSH}$ ) as a reducing agent capable of reducing the di-iodide precursor, the reduced species then, as we have seen, readily displacing  $\text{I}^-$ . The liberated  $\text{I}^-$  is finally removed from the solution as HI (or, in fact,  $[\text{QH}_2]\text{I}$ ), there being a final combination of the radical Q with  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}](\text{solvate})$  to give the product. Earlier, we had found that formation of the amido and hydrazido species occurred most efficiently when two moles of N-base per mode of di-iodide were used, and, in fact, we frequently recovered  $[\text{RNH}_3]\text{I}$  or  $[\text{RR}'\text{NNH}_3]\text{I}$  as a by-product.



Scheme 5

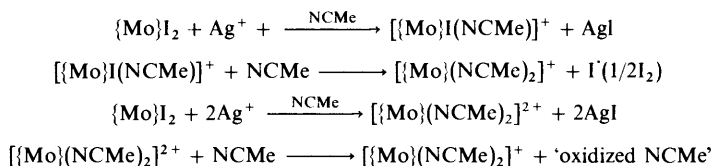
However, the reaction of  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}_2]$  with alcohols is a little more difficult to envisage in terms of a redox reaction. There are at least 1000 mV separating the oxidation potential of ethanol from that of the di-iodide. Bearing in mind that the formation of the alkoxides most often occurs in the neat alcohol as solvent as well as reactant, we may speculate that the reduction wave of the di-iodide is actually overlapped by the oxidation wave of the alcohol. So, as the concentration of the di-iodide is relatively small, conversion into the reduced species, followed by  $\text{I}^-$  loss which, as we had earlier observed, is facilitated by traces of water, could occur, and the monoalkoxides would result. However, this is not a very satisfactory explanation, especially as, under certain circumstances, bis-alkoxides are formed, and we know that the reduction potentials of  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}(\text{OR})]$  are significantly more negative relative to that of the di-iodide. The generality of this mechanism must also be questioned with respect to the reactions of  $[\text{W}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{Cl}_2]$ , and, in fact, a careful kinetic study of these reactions is in progress.



Scheme 6

Another puzzling observation concerns the behaviour of  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}_2]$  with  $\text{Ag}^+$ . We had used  $\text{AgOAc}$  to facilitate a number of reactions on the basis of the principle that acetate is a good leaving group, as we had found with  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{I}(\text{OAc})]_2$ , *viz.* Scheme 6. We did notice, from time-to-time, that

there were reactions with AgOAc other than those we desired but chose, in the event of success in the intending direction, to ignore them. However, when  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}_2]$  was treated with  $\text{AgPF}_6$  in acetonitrile, Gianfranco Denti and Mauro Ghedini obtained the *mono-cation*  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})(\text{NCMe})_2][\text{PF}_6]$ , whether they used one or two mole equivalents of  $\text{Ag}^+$ . They had expected to produce the *di-cation* but instead isolated, and characterized crystallographically, this green-brown paramagnetic ( $g = 1.982$  in MeCN) complex.<sup>56,57</sup> The formation of this mono-cation formally corresponds to a *reduction* of the di-iodide (the unpaired electron resides predominantly in a metal-based orbital) in the presence of an oxidizing agent ( $\text{Ag}^+$ )! During the work-up of the product the formation of  $\text{I}_2$  was observed, and, at the moment, we view the overall reaction as shown in Scheme 7. From preliminary studies, it appears that certain N-heterocycles behave similarly.



Scheme 7

During a study of the behaviour of  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}_2]$  with  $\alpha,\omega$ -diols, which will be described later, Andrzej Włodarczyk noticed that the di-iodide reacted with acetone which, up to that point, had been a favourite reaction solvent. After a great deal of very hard and skilful work, Andrzej and Gianfranco Denti, succeeded in isolating three species from the reaction with acetone.<sup>58</sup> These were a bicyclic organic cation  $[\text{C}_6\text{H}_3\text{Me}_5\text{N}_2(\text{OH})]^+$ , obtained as either a mono-iodide or a mixture of mono- and tri-iodide, a bimetallic  $\mu$ -oxo species  $[ \{\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}_2\text{O} ]$ , and  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}(\text{OEt})]$ . All of these compounds were obtained in low yield and despite strenuous attempts, we were never able to identify any other molybdenum-containing products. The organic products obtained from the acetone reaction were diacetone alcohol, mesityl oxide, and water, but no ethanol. Similar products were obtained from reaction with diacetone alcohol, the organics being identified as the bicyclic cation mentioned above, traces of acetone, the original diacetone alcohol (much reduced in concentration), substantial amounts of mesityl oxide, and water, but *no* methanol or ethanol.

The formation of the cation  $[\text{C}_6\text{H}_3\text{Me}_5\text{N}_2(\text{OH})]^+$  (Figure 9), the nature of which was established crystallographically, was unexpected because we had always assumed that the  $\text{HB}(\text{Me}_2\text{pyz})_3$  liquid was relatively stable. However, boron has a high affinity for chelating oxygen-containing ligands, and it is conceivable that

<sup>56</sup> G. Denti, M. Ghedini, J. A. McCleverty, H. Adams, and N. A. Bailey, *Transition Met. Chem.*, 1982, 7, 222.

<sup>57</sup> N. M. Atherton, G. Denti, M. Ghedini, and C. Oliva, *J. Magn. Reson.*, 1981, 43, 167.

<sup>58</sup> H. Adams, N. A. Bailey, G. Denti, J. A. McCleverty, J. M. A. Smith, and A. Włodarczyk, *J. Chem. Soc., Dalton Trans.*, 1983, in press.

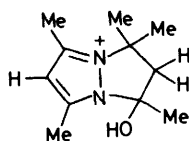


Figure 9

diacetone alcohol sequestered it, either as  $[B(OCMe_2CH_2COMe)_2]^+$  or  $[B(OCMeCHCOMe)_2]^-$ , although we could never confirm this. However, we had earlier established that *o*-catechol reacted with  $[Mo\{HB(Me_2pyz)_3\}(NO)I_2]$  affording<sup>59</sup>  $[Mo(Me_2pyz)_3(NO)(O_2C_6H_4)]I_3$ , whose structure was also elucidated by X-ray methods (Figure 10). This deboronation reaction proceeded in good yields and we presume that one of the major by-products must be  $[B_2(O_2C_6H_4)_3]$  or  $[B(O_2C_6H_4)_2]^-$ , although, again, we were unable to confirm this. In the deboronation reaction, dimethylpyrazole must be released, and could react with mesityl oxide, as shown in Scheme 8, to give the bicyclic cation. Addition of pyrazoles to  $\alpha,\beta$ -unsaturated carbonyl compounds is known,<sup>60</sup> but so far as we are aware, 1,4-cycloaddition of this particular type is new.

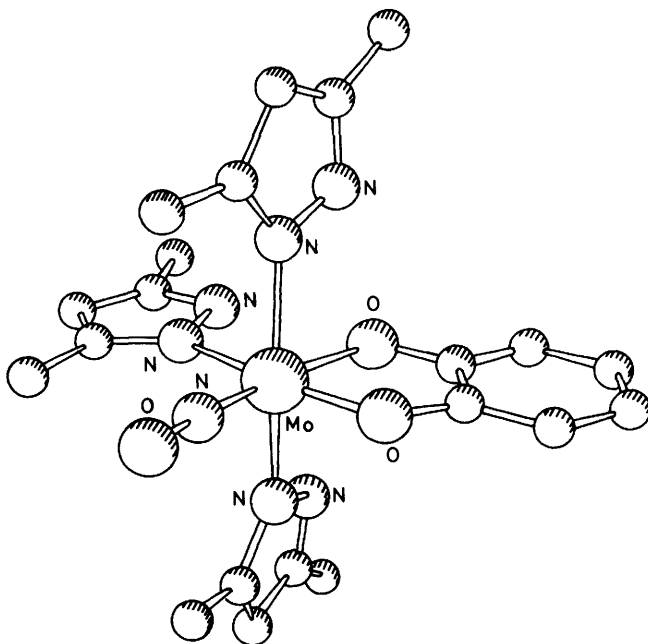
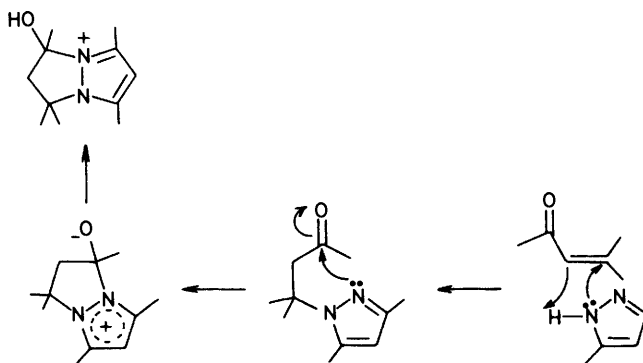


Figure 10

<sup>59</sup> H. Adams, N. A. Bailey, A. S. Drane, and J. A. McCleverty, *Polyhedron*, 1983, 465.

<sup>60</sup> R. H. Wiley, N. R. Smith, D. M. Johnson, and J. Moffatt, *J. Am. Chem. Soc.*, 1955, 77, 2572.



Scheme 8

The structure of the bimetallic complex  $[\{\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}_2\text{O}]$  (Figure 11) was also established crystallographically.<sup>58</sup> It is an interesting molecule, being severely overcrowded, but exhibiting relatively short Mo—O distances (1.86 and 1.93 Å) which are comparable to those in the alkoxy species  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{X}(\text{OR})]$  (1.86–1.92 Å). Furthermore, the Mo—O—Mo bond is slightly bent ( $171^\circ$ ) which is in contrast to most other molybdenum complexes containing a single  $\mu$ -oxo bridge, where, because of extensive  $\pi$ -bonding in the Mo—O—Mo system, linearity is expected. This distortion from linearity must arise from steric restraints imposed by the proximity of the two very bulky  $\text{HB}(\text{Me}_2\text{pyz})_3$  ligands.

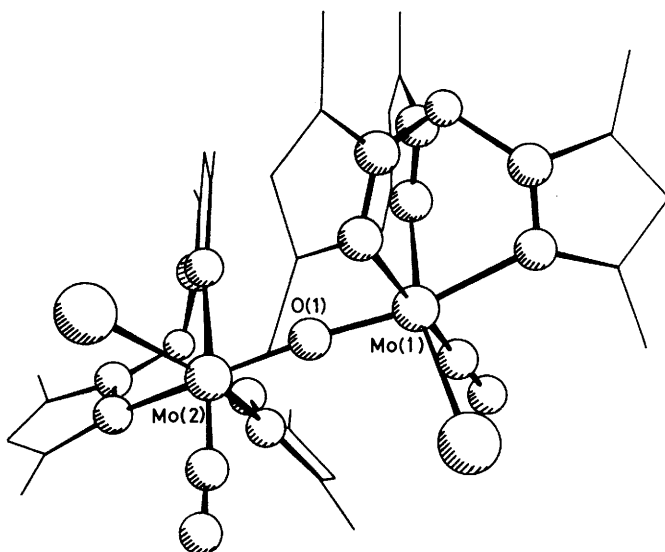


Figure 11



The formation of this bimetallic is not easy to understand. Certainly water is present in the reaction (from acid- or base-catalysed dehydration of diacetone alcohol), and could react with  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}_2]$  giving the known  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}(\text{OH})]$ .<sup>29</sup> The mono-hydroxide could then react with more di-iodide, affording the  $\mu$ -oxo species. However, we have not been able to achieve this in trial experiments.

We have also noticed that during recrystallization of  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}_2]$  from toluene in air, small amounts of the  $\mu$ -oxo species are produced. However, we have established that  $\text{O}_2$  is not apparently responsible for this, so the mechanism of formation of the binuclear compound remains a mystery.

Just as puzzling is the formation of  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}(\text{OEt})]$ . To generate an *ethoxide* from acetone and/or diacetone alcohol requires C—C bond cleavage! We would have expected that acetone could reduce the precursor di-iodide giving  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}_2]^-$ , as described earlier. However, the concomitant one-electron oxidation of acetone would not be expected to lead to ethoxide formation: normally methyl or acetyl radicals, or even  $\cdot\text{CH}_2\text{COME}$ , would be formed.<sup>61</sup> It is possible that enolization of acetone, followed by elimination of HI from the di-iodide precursor, could give the transient  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{IOC}(\cdot\text{CH}_2)\text{Me}]$  which might then undergo hydrolysis of the methylene group affording the ethoxide and formaldehyde. However, we were unable to detect  $\text{C}_1$ - or  $\text{C}_2$ -derived reaction products. We are entirely confident, however, that ethanol is *not* present in either the reaction or the crystallization solvents.

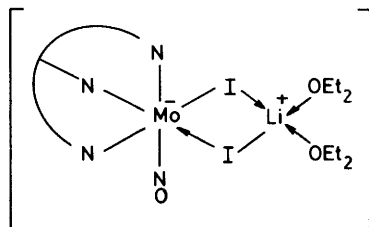
Prior to our electrochemical studies of  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}_2]$ , Krystyn Tyrlik had tried to reduce the compound with a variety of reagents, *e.g.* sodium naphthalenide, Na/Hg, and even Mg in THF.<sup>62</sup> In every case he observed almost complete disruption of the molecule, and was able to isolate only fragments, including dimethylpyrazole. Similar treatment of  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})(\text{CO})_2]$  also led to the destruction of the molecule, although on some occasions we observed the formation of species apparently containing NCO, perhaps formed by reaction, under reducing conditions, between co-ordinated NO and CO. Such reactions are known,<sup>2</sup> but we were unable to characterize the compound. Later, Nigel Briggs, in attempting to make  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}(\text{Ar})]$ , where Ar = Ph or *p*-MeC<sub>6</sub>H<sub>4</sub>, by treating the di-iodide with LiAr in ether, isolated beautiful magenta crystals.<sup>63</sup> These crystals, made in several different ways many times, resolutely refused to diffract properly, so we were unable to identify the compound crystallographically. We noted that the compound reacted with ethanol affording  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}(\text{OEt})]$  and the corresponding bis-ethoxide, with benzyl bromide affording  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{Br}_2]$ , and with CO giving  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})(\text{CO})_2]$ . It was not until we compared the electro-

<sup>61</sup> 'Organic Reaction Mechanisms', 1977, 127; 1978, 141; M. O. Kano and T. Aratani, *Bull. Chem. Soc. Jpn.*, 1967, **49**, 4811; M. G. Vinogradov, S. P. Verenchikov, and G. I. Nikishin, *Zh. Org. Khim.*, 1976, **12**, 527 and 2245.

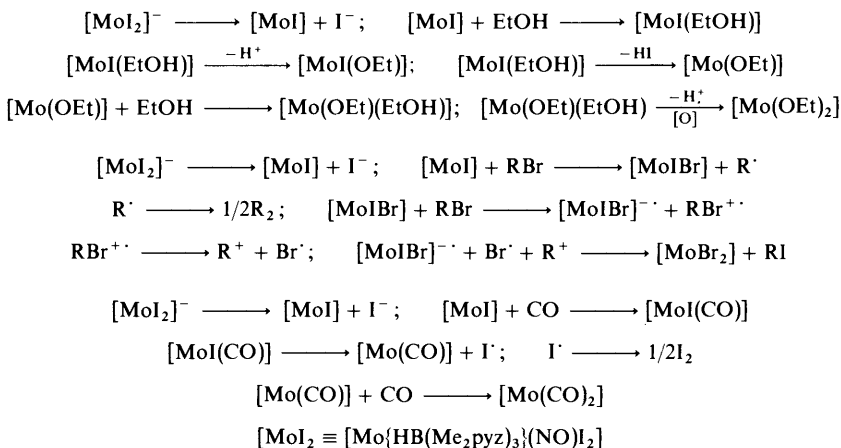
<sup>62</sup> S. K. Tyrlik and J. A. McCleverty, unpublished work.

<sup>63</sup> T. N. Briggs, N. H. Colquhoun, C. J. Jones, J. A. McCleverty, and B. D. Neaves, work to be published.

chemistry of this magenta complex (which became green in THF!) with that of  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}_2]$ , that we realised that we had probably formed a salt of  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}_2]^-$ .<sup>54,55</sup> Having compared the e.s.r. spectrum of this magenta compound with that of electrochemically reduced di-iodide, we established that they were identical. Elemental analyses of the magenta complex were entirely consistent with the formulation  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}_2\text{Li}(\text{OEt}_2)_2]$  and we propose that it has the structure shown in Figure 12, which would make it analogous to  $[\text{Yb}(\eta\text{-C}_5\text{Me}_5)_2\text{I}_2\text{Li}(\text{OEt}_2)_2]$ .<sup>64</sup> The reactions with ethanol, benzyl bromide, and CO could then be rationalized as shown in Scheme 9.



**Figure 12**



**Scheme 9**

The facility with which  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}_2]$  could be reduced to a paramagnetic mono-anion encouraged Sarah Reynolds and Bryan Neaves to carry out an extensive survey of the general electrochemical behaviour of the mono-substituted species  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{XY}]$ , where  $\text{M} = \text{Mo}$  and  $\text{X} = \text{Q}$  or  $\text{I}$ , and  $\text{M} = \text{W}$  and  $\text{X} = \text{Cl}$ . Their results have shown that all complexes undergo at least one one-electron reduction in acetonitrile or THF. This has been established

<sup>64</sup> P. L. Watson, *J. Chem. Soc., Chem. Commun.*, 1980, 652.

by cyclic voltammetry and coulometry. The  $E_{1/2}$ -values for the reduction wave depends both on the metal atom, W complexes being reduced at potentials *ca.* 500 mV more cathodic than their Mo analogues, and on the donor atoms and their substituents. Typically, molybdenum iodo-phenoxides reduce at *ca.*  $-0.3$  V (*vs.* SCE), iodo-alkoxides at *ca.*  $-0.6$  V, and iodo-arylamides at *ca.*  $-0.9$  V. In the case of phenoxides and arylamides, the exact value of  $E_{1/2}$  also depends on the substituents present on the aromatic ring. So far, our most comprehensive data have been obtained<sup>55</sup> for complexes of the type  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}(\text{NHC}_6\text{H}_4\text{-}p\text{-Z})]$ , where Z is one of a variety of substituents ranging from electron-releasing to electron-withdrawing. There is a broadly linear correlation between the Hammett  $\sigma$  *para* substituent constant for Z and the  $E_{1/2}$ -value for the complex. The line has a slope of  $-400$  mV so that the most electron-releasing Z groups give rise to the most cathodic  $E_{1/2}$ -values. A coupled chemical reaction, which can be shown by peak matching methods to be dissociation of  $\text{I}^-$  from the reduced complex, is observed for all Z groups. This halide dissociation is absent, however, in all species of the type  $[\text{M}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{ClY}]$  and in the molybdenum iodo-phenoxides.

The fact that the basic unit  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{XY}]$  is redox-active induced us to think about the possibilities of attachment to other metal centres, thereby generating a hetero-, bi- or tri-metallic system which might have extensive electrochemical activity. In such a mixed-metal system, we wondered whether the redox-active metal-centre would act as a 'switch' to control the reactivity of another metal. We therefore set ourselves the task of designing homo- and hetero-, bi- or tri-metallic metal complexes in which the tris-pyrazolyl-borato molybdenum, or tungsten, moiety could be linked to another metal system which might or might not itself be redox active. We intended that there should be no direct metal-metal bond between Mo or W and the other metal and, clearly, this was going to be unlikely on steric grounds. However, we could see the possibility that Mo or W could be attached to the new metal *via* a conjugated or delocalized bridging system, or *via* a non-conjugated or 'insulating' link.

In order to achieve the connection of the tris-pyrazolylborato complexes to another metal, we first had to prepare monometallic complexes functionalized so as to bond to the new metal. This could be achieved by attachment of a potentially bifunctional ligand, *e.g.*  $\text{HO}(\text{CH}_2)_n\text{OH}$  ( $n = 2-4$ ),  $\text{NH}_2(\text{CH}_2)_3\text{PPh}_2$ ,  $p\text{-HOC}_6\text{H}_4\text{OH}$ , or  $p\text{-NH}_2\text{C}_6\text{H}_4\text{I}$  *via* one donor atom (N or O) to  $[\text{M}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{X}_2]$ . Liz Rae had found<sup>65</sup> that  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}_2]$  reacted readily with ethanolamine forming the simple amido-complex  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}(\text{NHCH}_2\text{CH}_2\text{OH})]$ . Andrzej Włodarczyk and Gianfranco Denti subsequently established that  $\alpha,\omega$ -diols would react with  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}_2]$  to give only mono- and bis-alkoxides in which the diol was exclusively mono-dentate with respect to the metal.<sup>66</sup> There was absolutely no evidence for the formation of chelate ring systems of the type  $\text{Mo}-\text{O}(\text{CH}_2)_n\text{O}$ .

<sup>65</sup> J. A. McCleverty, A. E. Rae, I. Wlochowicz, N. A. Bailey, and J. M. A. Smith, *J. Organomet. Chem.*, 1979, **168**, C1.

<sup>66</sup> G. Denti, J. A. McCleverty, and A. Włodarczyk, *J. Chem. Soc., Dalton Trans.*, 1981, 2021.

Gianfranco further established that *p*-substituted hydroxy- or amino-phenols and anilines readily formed monomeric species such as  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}(\text{NHC}_6\text{H}_4\text{NH}_2)]$  and Sarah Reynolds was able to prepare  $[\text{M}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{XNH}(\text{CH}_2)_3\text{PPh}_2]$  ( $\text{M} = \text{Mo}$ ,  $\text{X} = \text{I}$ ;  $\text{M} = \text{W}$ ,  $\text{X} = \text{Cl}$ ).<sup>55</sup>

The next step, formulation of bimetallic species, could be achieved in a number of ways, although so far we have used only three techniques.<sup>55</sup>

- (a) Reaction of a 'metallo-amine' or 'metallo-alcohol/phenol' with  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{X}_2]$ , thereby forming homo- and hetero-bimetallic complexes. Thus, addition of purple  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}(\text{NHC}_6\text{H}_4\text{NH}_2)]$  to  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}_2]$  in solution afforded the deep blue  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}(\text{NHC}_6\text{H}_4\text{NH})\text{MoI}(\text{NO})\{\text{HB}(\text{Me}_2\text{pyz})_3\}]$ , abbreviated  $[\{\text{MoI}\}(\text{NHC}_6\text{H}_4\text{NH})\{\text{MoI}\}]$ . Similarly, treatment of orange  $[\text{W}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{Cl}(\text{NHC}_6\text{H}_4\text{OH})]$  with  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}_2]$  afforded the deep orange-brown heterobimetallic  $[\{\text{WCl}\}(\text{NHC}_6\text{H}_4\text{O})\{\text{MoI}\}]$ .
- (b) Reaction of a complex containing *p*-halide atoms in an aromatic derivative with co-ordinatively unsaturated compounds, *via* oxidative addition. For example,  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}(\text{NHC}_6\text{H}_4\text{I})]$  reacted with  $[\text{Pd}(\text{PPh}_3)_4]$  affording the purple heterobimetallic species  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}\{\text{NHC}_6\text{H}_4\text{PdI}(\text{PPh}_3)_2\}]$ , and similar Pt-containing complexes were prepared.
- (c) Reaction of 'metallo-phosphine' complexes with metal halides. Thus  $[\text{W}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{ClNH}(\text{CH}_2)_3\text{PPh}_2]$  reacted with  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  giving the trimetallic  $[\{\text{W}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{Cl}\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ , abbreviated  $[\text{Rh}(\text{CO})\text{Cl}\{\text{PPh}_2\text{-WCl}\}_2]$ , while  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}\{\text{NH}(\text{CH}_2)_3\text{PPh}_2\}]$  reacted with  $\text{HgI}_2$  giving  $[\text{HgI}_2\{\text{PPh}_2\text{-MoI}\}_2]$ .

Knowing that the nitrosyl metal tris-pyrazolylborate system was intrinsically redox-active, we have made our primary concern the electrochemical examination of the bimetallic species formed *via* route (a). All of the complexes underwent at least one one-electron reduction in acetonitrile or THF. Some undergo two one-electron reductions and often these electrode processes are reversible, especially the less cathodic ones, when  $E_{1/2} < -0.6$  V, and when the complexes contain phenolic groups and/or chloride attached to the metal. Although our work is in its preliminary stages, the data provide evidence for strong, intermediate, or weak interactions between the metal centre, depending on the nature of the bridging ligand. These data are summarized in Table 3. In symmetrical homo-bimetallic complexes in which  $-\text{CH}_2-$  or  $-\text{CH}_2\text{CH}_2-$  groups link the two halves of the molecule, a single broad two-electron reduction wave is observed at potentials virtually identical to those detected for the related mono-metallic species, *e.g.*  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}(\text{NHPH})]$ ,  $E_{1/2} = -0.83$  V. In fact a 36 mV separation would be expected on statistical grounds if both redox centres in the homo-bimetallic species had identical  $E_{1/2}$ -values,<sup>67</sup> but we cannot detect this with our equipment. Thus there is *no* electrochemically detectable interaction between the metal centres in such systems. If, instead, the two halves of the molecule are linked by O, S, or  $\text{SO}_2$  groups, two overlapping waves are observed by cyclic voltammetry, and the two reduction processes are separated by *ca.* 100 mV in each case. As the

<sup>67</sup> J. B. Flanagan, S. Margal, A. J. Bard, and F. C. Anson, *J. Am. Chem. Soc.*, 1978, **100**, 4248.

**Table 3** Reduction potentials for bimetallic complexes and their monometallic analogues

Complex <sup>a</sup>	$E_{1,2}$ /volts <sup>b</sup>	$\Delta E_p$ /mV
NHC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	-0.85	60
{Mo}NHC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH{Mo}	-0.84 <sup>c</sup>	150
{Mo}NHC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	-0.85	80
{Mo}NHC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH{Mo}	-0.84 <sup>c</sup>	120
{Mo}NHC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	-0.54	80
{Mo}NHC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH{Mo}	-0.49	60
	-0.60	80
{Mo}NHC <sub>6</sub> H <sub>4</sub> OC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	-0.86	70
{Mo}NHC <sub>6</sub> H <sub>4</sub> OC <sub>6</sub> H <sub>4</sub> NH{Mo}	-0.88 <sup>c</sup>	240
{W}NHC <sub>6</sub> H <sub>4</sub> OC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	-1.30	100
{W}NHC <sub>6</sub> H <sub>4</sub> OC <sub>6</sub> H <sub>4</sub> NH{W}	-1.32 <sup>c</sup>	160
{Mo}NHC <sub>6</sub> H <sub>4</sub> OC <sub>6</sub> H <sub>4</sub> NH{W}	-0.81	70
	-1.37 <sup>b</sup>	—
{Mo}NHC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	-0.98 <sup>b</sup>	—
{Mo}NHC <sub>6</sub> H <sub>4</sub> NH{Mo}	-0.48	60
	-1.52 <sup>d</sup>	—
{W}NHC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	-1.44	120
{W}NHC <sub>6</sub> H <sub>4</sub> NH{W}	-1.16	80
	-1.72 <sup>d</sup>	—
{Mo}NHC <sub>6</sub> H <sub>4</sub> NH{W}	-0.74	60
	-1.66 <sup>d</sup>	—
{Mo}NHC <sub>6</sub> H <sub>4</sub> OH	-1.01 <sup>d</sup>	—
{Mo}NHC <sub>6</sub> H <sub>4</sub> O{Mo}	-0.15	100
	-1.16	70
{Mo}NHC <sub>6</sub> H <sub>4</sub> O{W}	-0.28	70
	-1.60 <sup>d</sup>	—

<sup>a</sup> {Mo} = {HB(Me<sub>2</sub>pyz)<sub>3</sub>}Mo(NO)I, {W} = {HB(Me<sub>2</sub>pyz)<sub>3</sub>}W(NO)Cl. <sup>b</sup> For a 1-electron process unless otherwise stated. <sup>c</sup> 2-electron process, broadened wave observed. <sup>d</sup>  $E_p$  reduction quoted—oxidation peak shifted by a chemical reaction following the reduction.

potential separation between two successive reductions becomes less than 100 mV the individual waves merge into one distorted wave.<sup>68</sup> Where the two metal centres are more directly linked, for example by —NHC<sub>6</sub>H<sub>4</sub>NH—, —OC<sub>6</sub>H<sub>4</sub>O—, or —NHC<sub>6</sub>H<sub>4</sub>O— bridging ligands, two one-electron reduction processes are observed. The potentials of these processes straddle that of the related monometallic species and suggest a interaction between the metal centres.

A similar state of affairs exists for the hetero-bimetallic species, except that two one-electron processes are observed, corresponding to reduction at each of the two different metal centres. The potentials of these processes again differ from those of the related monometallic species by an amount dependent on the extent to which the metal centres influence one another.

<sup>68</sup> D. Polcyn and I. Shain, *Anal. Chem.*, 1966, **38**, 370, 376.

If we accept that the relationship between  $E_{1/2}$  and the Hammett  $\sigma$  *para* constant in the arylamido systems is valid, then it is possible to assign  $\sigma$  *para* values to the metal centres on the basis of the  $E_{1/2}$ -values of the bimetallic compounds. In this way  $\sigma$  *para* values of +0.83, +0.20, -0.81, and -1.74 may be assigned respectively to the substituents  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{INH}-]$ ,  $[\text{W}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{CINH}-]$ ,  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{IO}-]^-$  and  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{INH}-]^-$ . These figures suggest that the replacement of a *p*-amino hydrogen atom by a molybdenum centre in  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}(\text{NHC}_6\text{H}_4\text{NH}_2)]$  exerts a powerful electron-withdrawing effect on the original metal atom. However, once an Mo centre has been reduced, it appears to become powerfully electron-releasing towards the unreduced metal.

All of these observations lead us towards an eventual goal of using the redox properties of one metal-centre to act as a 'switch' to control the reactivity of another. In complexes prepared by route (c), for example, a reduced Mo-centre might be used to activate the second metal towards oxidative addition reactions. Subsequent oxidation of the Mo might then promote a reductive elimination in which a functional group on the original reactant is exchanged with a ligand on the metal. It seems from our current work that the most useful complexes for carrying out such a study are derived from phenolic species, and consequently we are now exploring the chemistry of  $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pyz})_3\}(\text{NO})\text{I}(\text{OC}_6\text{H}_4\text{PPh}_2)]$  and related compounds.

We also hope to establish the extent of electron delocalization in the so-called 'mixed valence' species derived from our homo- and hetero-bimetallics. We can only do this effectively using e.s.r. techniques and by measuring the 'inter-valence' bands in the near infrared. Again, the ideal species for this work are those containing phenolic bridges, and an isolation and detailed study of the reduced species will allow us to make a meaningful comparison of our complexes with the interesting 'valence trapped' species based on  $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$  prepared by Taube *et al.*<sup>69</sup>

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<sup>69</sup> P. Ford, R. Gaunder, DeF. P. Rudd, and H. Taube, *J. Am. Chem. Soc.*, 1968, **90**, 1187; C. Creutz and H. Taube, *ibid.*, 1973, **95**, 1086 and 1969, **91**, 3988; H. Fischer, G. M. Tom, and H. Taube, *ibid.*, 1976, **98**, 5512; K. Rieder and H. Taube, *ibid.*, 1977, **99**, 7891; J. E. Sutton, P. M. Sutton, and H. Taube, *Inorg. Chem.*, 1979, **18**, 1017; J. E. Sutton and H. Taube, *ibid.*, 1981, **20**, 3125.