

Preliminary communication

**HETERO-BI- AND TRI-METALLIC COMPLEXES CONTAINING BOTH
 ELECTRON RELEASING AND ELECTRON ACCEPTING REDOX
 CENTRES ***

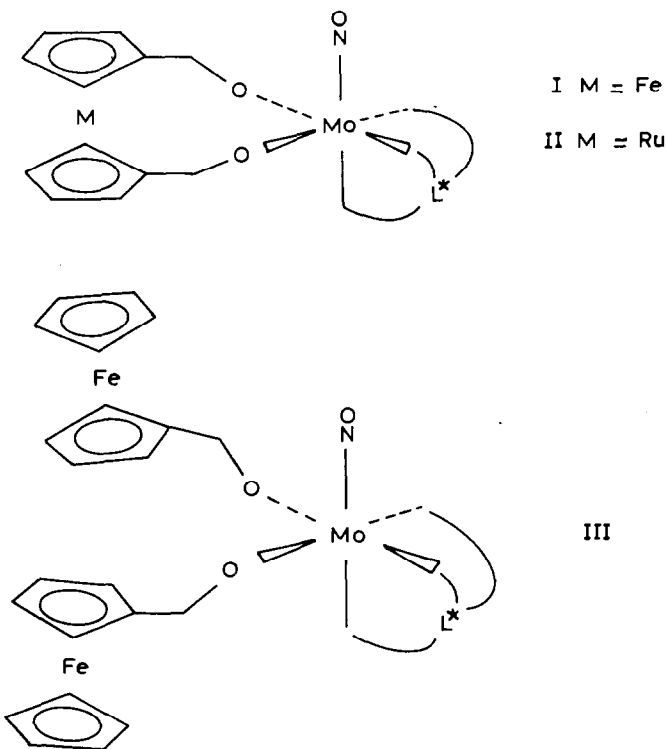
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Summary

The new complexes $[M(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{O})_2\text{Mo}(\text{NO})\text{L}^*]$; $M = \text{Fe}$ or Ru and $\text{L}^* =$ (hydro)tris(3,5-dimethylpyrazolyl)borate, which contain a chelating metallocene ligand, have been prepared and characterised along with the related trimetallic complex $[\{\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{O})\}_2\text{Mo}(\text{NO})\text{L}^*]$. Their electrochemical properties are reported, and the reduction potentials for the $\{\text{Mo}(\text{NO})\}^{4+}$ redox centre in the chelated species are 100 mV more anodic than for that in the trimetallic non-chelated complex.

The sterically-demanding tripodal ligand $\{\text{HB}(3,5\text{-Me}_2\text{C}_3\text{N}_2\text{H})_3\}^-$, L^* , restricts the coordination spheres of metals to which it is bound so that only complexes having essentially octahedral or tetrahedral geometries may form. In the case of the $\{\text{Mo}(\text{NO})\}^4$ core this results in the formation of formally 16-electron complexes of formula $[\text{Mo}(\text{NO})\text{L}^*\text{XY}]$ in which X and/or Y is halide, amide, alkoxide or thiolate. These electron deficient compounds undergo one-electron reduction reactions at potentials which vary substantially depending on the nature of X and Y [1,2]. Thus the reduction potentials of the complexes $[\text{Mo}(\text{NO})\text{L}^*\text{Cl}\{\text{NHC}_6\text{H}_4\text{Z}\}]$, in which Z is one of a variety of *para* substituents, are linearly related to the substituent constant, σ_p , with a reaction constant of 6.7 [3,4]. We have further found that in homobimetallic complexes, $[\{\text{Mo}(\text{NO})\text{L}^*\text{Cl}\}_2(\text{BL})]$ (BL = a bifunctional bridging ligand) the two metal centres may influence one another to an extent which varies according to the nature of the bridging ligand which links them [3,5–7]. Thus when the bridging ligand is *para*-OC₆H₄O or *para*-NHC₆H₄NH the metal centres interact strongly and two well separated one electron reduction processes are observed. However, when saturated bridges are used, as in *para*-OCH₂C₆H₄CH₂O or *para*-NHC₆H₄CH₂C₆H₄NH for example, there is negligible interaction between

* Dedicated to Prof. G.E. Coates on the occasion of his 70th birthday.



the metal centres as determined electrochemically, and they exhibit a single two-electron reduction process.

When the bridging ligand itself contains a metallocene redox centre the two $\{\text{Mo}(\text{NO})\}^4$ cores may still influence one another. In the case of $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{SMo}(\text{NO})\text{L}^*\text{Cl}\}_2]$ the Mo–Mo interaction is similar in magnitude to that found with *meta*- $\text{SC}_6\text{H}_4\text{S}$ as the bridging ligand [8]. This interaction is substantially larger than that between the ruthenium centres in $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{CNRu}(\text{NH}_3)_5\}_2]^{4+}$ (two one electron reductions separated by 250 mV as opposed to no detectable interaction and a single reduction wave for the Ru derivative) [9]. We have now extended our studies of complexes containing both $\{\text{Mo}(\text{NO})\text{L}^*\text{X}$ and metallocene redox centres to include examples where two redox centres are held in close proximity by essentially “insulating” bridging ligands. The object of this work is to determine whether substantial through space interactions might occur between the metallocene and the molybdenum redox centres.

The dialcohols 1,1'-bis(hydroxymethyl)ferrocene and its ruthenium analogue were prepared by previously reported methods [10]. These compounds were treated in 1/1 molar ratio with $[\text{Mo}(\text{NO})\text{L}^*\text{I}_2]$ in the presence of triethylamine to give the pink products **1** and **2** in 39 and 42% yields, respectively. The compounds were purified by column chromatography, **1** was also prepared in 50% yield from the reaction between 1,1'-bis(hydroxymethyl)ferrocene and $[\text{Mo}(\text{NO})\text{L}^*\text{I}(\text{OEt})]$ in the presence of NEt_3 . The trimetallic complex $[\{\text{Mo}(\text{NO})\text{L}^*\}\{(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{O})\text{Fe}\}_2]$ (**3**) was prepared by the reaction of hydroxymethylferrocene [11] in 2/1 molar ratio with $[\text{Mo}(\text{NO})\text{L}^*\text{I}_2]$ in the presence of NEt_3 . The red product

TABLE 1
SELECTED INFRARED AND ELECTROCHEMICAL DATA

Complex	NO Frequency ^a (cm ⁻¹)	E _{1/2} ^b (V)	ΔE _p ^c (mV)
[Fe(η ⁵ -C ₅ H ₄ CH ₂ O) ₂ Mo(NO)L*]	1643	+0.39 -1.39	110 (110) 220
[Ru(η ⁵ -C ₅ H ₄ CH ₂ O) ₂ Mo(NO)L*]	1640	+1.05 ^d -1.39	-(160) 210
[(Fc(η ⁵ -C ₅ H ₅)(η ⁵ -C ₅ H ₄ CH ₂ O)) ₂ Mo(NO)L*]	1630	+0.38 ^e -1.49	180 (115) 190
[Mo(NO)L*(OCH ₂ Ph) ₂]	1632	-1.34	230 (160)

^a KBr disc. ^b Obtained from cyclic voltammetry studies in dichloromethane solvent containing 0.2 M [Buⁿ₄N]BF₄ as supporting electrolyte. Solutions were ca. 2 × 10⁻³ M in complex and measurements were made at 21 ± 1 °C at 0.2 V s⁻¹ scan rate using a Pt bead working electrode with Fc^{0/+} internal reference. Values are quoted relative to the saturated calomel reference electrode. ^c Separation between anodic and cathodic peak potentials, values for ferrocene under the same conditions in parentheses. No compensation was made for internal cell resistance. Generally ΔE_p decreased with scan rate but at 20 mV s⁻¹ was similar to that of the reference couple indicating a kinetically controlled electron transfer process. ^d Anodic peak potential for an irreversible process. ^e Two electron process for two one electron transfers at similar potentials. All other electron transfers were one electron processes on the basis of the current function for [Mo(NO)L*Cl₂] in the same cell and the known redox behaviour of the metallocene and {Mo(NO)}⁴ redox centres.

was isolated in 43% yield and purified by column chromatography. All the new compounds were characterised by infrared, ¹H NMR, ¹³C NMR and mass spectroscopy. All gave elemental analyses in accord with their formulations and exhibited nitrosyl stretching frequencies in the region associated with bis-alkoxide derivatives of {Mo(NO)L*}, as shown in Table 1.

The electrochemical properties of the new compounds were investigated in dichloromethane solution by cyclic voltammetry and the results are summarised in Table 1. Except for the ruthenium oxidation process in **2**, all the electron transfer processes were chemically reversible on the cyclic voltammetry time scale. However the shape parameter ΔE_p was generally larger than for the internal standard, suggesting that the electron transfer process was kinetically controlled. The reduction potentials of the molybdenum centres are in accord with their formulations as bis-alkoxide derivatives.

A comparison of the reduction potentials of **1** and **2** shows that the replacement of Fe by Ru has no effect on the reduction potential of the molybdenum redox centre. In the case of **3** the ferrocene moieties were oxidised in a single two electron process, indicating that the iron atoms were not influencing one another to an electrochemically detectable extent through the molybdenum-containing bridge system. This result is in accord with expectation, since the bridge ligand contains "insulating" CH₂ units.

The replacement of the two OCH₂Ph ligands in [Mo(NO)L*(OCH₂Ph)₂] by (η⁵-OCH₂C₅H₄)Fe(η⁶-C₅H₅), to give **3**, results in a cathodic shift of 150 mV in the reduction potential of the {Mo(NO)}⁴ redox centre. This may be attributed to the effect of replacing the neutral phenyl substituent of the alkoxide ligand with a cyclopentadienyl group bearing a putative negative charge. The reduction potential of **1**, in which the metallocene unit is held in close proximity to the molybdenum

centre by chelate formation, is 100 mV more anodic than in **3**. Further work is in progress to establish unequivocally whether this effect is due to through-space interactions. However, these preliminary results would be in accord with the 18-electron ferrocene unit having a modest stabilising effect on the reduced $\{\text{Mo}(\text{NO})\}^5$ core in the chelate **1** compared to that in the non-chelate derivative **3**.

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