

Preliminary communication

THE SYNTHESIS OF A NOVEL TRIMETALLIC COMPLEX CONTAINING THREE REDOX CENTRES AND AN ASSESSMENT OF INDUCTIVE EFFECT TRANSMISSION THROUGH AN IRON ATOM

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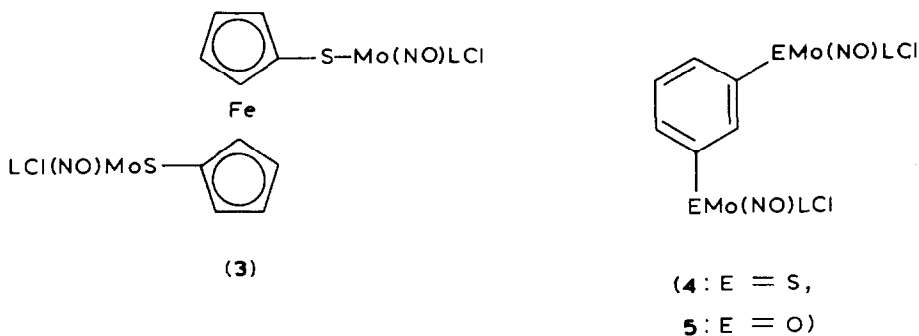
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Summary

The novel trimetallic complex $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{SMo}(\text{NO})\text{LCl}\}_2]$; in which L = tris(3,5-dimethylpyrazolyl)hydroborate, and its bimetallic analogue $[\{\text{Mo}(\text{NO})\text{LCl}\}_2(m\text{-S}_2\text{C}_6\text{H}_4)]$ have been synthesised; electrochemical studies of these compounds indicate that the inductive effects of the molybdenum-containing substituents are transmitted to equal extents through the C—Fe—C and C—C—C bridging atom chains.

There is now a substantial body of data relating to the transmission of substituent effects through organic moieties, especially through aryl rings [1]. However, information relating to transmission through compounds containing transition metal ions is more limited and is often based on non-equilibrium measurements [2]. Electrochemical studies of redox active metal centres can provide equilibrium data about the effects of ligand substituents on the properties of the metal itself [2, 3]. However, an electrochemical study of $[\{\text{NH}_3\}_5\text{Ru}\}_2\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CN})_2\}]^{4+}$ showed only weak interaction between the ruthenium redox centres and no clear assessment of the inductive effect transmission through iron was possible [4]. The situation was also complicated by the formation of mixed valence species involving both the iron and ruthenium centres, since all three centres underwent oxidation reactions. This problem may be avoided if the terminal substituents exhibit reduction rather than oxidation processes in their electrochemistry. Previous work in our laboratory has established that inductive interactions between redox-active molybdenum or tungsten centres which undergo reduction could be detected using cyclic voltammetry [5]. Thus the bimetallic complex $[\text{Mo}(\text{NO})\text{LI}(\text{NHC}_6\text{H}_4\text{NH})\text{Mo}$

(NO)LI], in which $L = \text{HB}(3,5\text{-Me}_2\text{C}_3\text{N}_2\text{H})_3$, exhibited a pronounced Mo—Mo interaction as evidenced by the observation of two one-electron reduction processes separated by ca. 1.0 V. In comparison the related complex $[\text{Mo}(\text{NO})\text{-LI}(\text{NHC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{NH})\text{Mo}(\text{NO})\text{LI}]$ exhibited a single broadened two-electron wave, indicating a negligible interaction between the molybdenum centres. We have now used this approach to investigate the transmission of inductive effects through the iron atom in a ferrocene derivative. This involved the synthesis of a novel trimetallic complex in which each cyclopentadienyl ring in ferrocene carried a redox active $\{\text{Mo}(\text{NO})\text{LCIS}\}$ substituent.



Ferrocene dithiol, $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{SH})_2]$ (1), was prepared using a previously reported method [6] and reacted, in 1/2 molar ratio, with $[\text{Mo}(\text{NO})\text{LCI}_2]$ (2), in the presence of sodium hydride. The purple product 3 was obtained in 66% yield and purified by column chromatography. A similar reaction was also carried out using benzene-1,3-dithiol and a maroon product 4 was obtained in 28% yield. The new trimetallic compound 3 and the bimetallic 4 were characterised by infrared, ^1H and ^{13}C NMR spectroscopy and gave elemental analyses consistent with their formulation as $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{S-Mo}(\text{NO})\text{LCI}\}_2]$ and $[\{\text{Mo}(\text{NO})\text{-LCI}\}_2(\text{S}_2\text{C}_6\text{H}_4)]$, respectively. Both complexes exhibited $\nu(\text{BH})$ at 2550 cm^{-1} in their infrared spectra, along with $\nu(\text{NO})$ at 1668 cm^{-1} for 3 and 1689 cm^{-1} for 4. The electrochemical properties of 3 and 4 were investigated by cyclic voltammetry in dichloromethane solution and the results obtained are presented in Table 1 and for 3 in Fig. 1. Some data for related complexes which have also been prepared and characterised in our laboratory [7], and for disubstituted ferrocenes prepared by previously reported methods [6], are also given for comparison.

These results indicate that the replacement of the sulphur atoms in 4 by oxygen produces little change in the reduction potentials of the molecule. Replacement of oxygen by sulphur might normally be expected to stabilise the lower oxidation state complex and produce an anodic shift in $E_{1/2}$. However, these complexes contain 16-electron molybdenum centres which appear to be stabilised by filled ligand $p\pi$ to empty metal $d\pi$ orbital charge donation. Under such circumstances the replacement of oxygen by a π -acceptor such as sulphur would not be expected to stabilise the reduced complex since this will still be electron deficient. Replacing the bridging aryl ring in 4 by ferrocenyl leads to a

TABLE 1

ELECTROCHEMICAL DATA

Complex	$E_{1/2}$ (V) ^a	ΔE_p (mV) ^b	$\Delta E_{1/2}$ (mV)
[Mo(NO)LCl(SPh)] [6]	-0.38	120	—
[Fe(η^5 -C ₅ H ₄ SH) ₂] [5]	+0.65	140	—
[Fe{(η^5 -C ₅ H ₄) ₂ S ₃ }] [5]	+0.85	100	—
[Fe{ η^5 -C ₅ H ₄ SMo(NO)LCl} ₂] (3)	-0.41	100	} 250
	-0.66	120	
	+0.78	120	
[{Mo(NO)LCl} ₂ (<i>m</i> -S ₂ C ₆ H ₄)] (4)	-0.31	100	} 240
	-0.55	140	
[{Mo(NO)LCl} ₂ (<i>m</i> -O ₂ C ₆ H ₄)] (5)	-0.32	100	} 260
	-0.58	120	

^a Obtained in CH₂Cl₂ solution at a Pt bead electrode using 0.2 M [Bu₄N]BF₄ as supporting electrolyte and 0.3 V s⁻¹ scan rate. All waves were reversible or quasireversible processes exhibiting well defined cathodic and anodic peaks. Coulometric measurements and comparisons with [Mo(NO)LCl₂] or ferrocene indicated that all were 1-electron processes. Potentials are quoted vs. SCE. ^b Difference between anodic and cathodic peak potentials, a typical value for ferrocene under similar conditions being 120 mV.

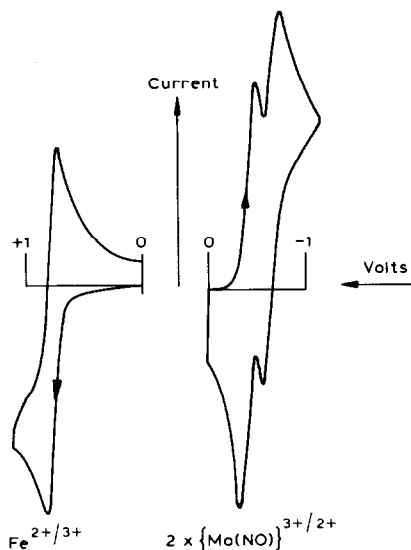


Fig. 1. Cyclic voltammogram of [Fe(η^5 -C₅H₄S{Mo(NO)LCl}₂)] (3).

cathodic shift of ca. 100 mV in both reduction potentials which presumably reflects the putative additional negative charge of the aromatic ring in C₅H₄S²⁻ as compared to C₆H₄S₂²⁻. The replacement of the thiol protons in [Fe(η^5 -C₅H₄SH)₂] by {Mo(NO)LCl}⁺ produces a modest anodic shift in the ferrocenyl oxidation potential. This shift is smaller than that induced by the inclusion of a bridging sulphur atom between the thiol groups to produce [Fe{(η^5 -C₅H₄)₂S₃}]. The most remarkable feature of the results obtained is the magnitude of the Mo—Mo interactions in 3, 4 and 5 as assessed by the difference between the first and second reduction potentials, $\Delta E_{1/2}$. Within the resolution of the electro-

chemical experiment these are effectively identical at 250 ± 10 mV. This finding indicates that the difference in the inductive effects of the $\{\text{Mo}(\text{NO})\text{LCIS}\}$ and $\{\text{Mo}(\text{NO})\text{LCIS}\}^-$ substituents is transmitted through the bridging C—C—C bond network of 4 and the C—Fe—C bond network of 3 to an equal extent.

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