Journal of Organometallic Chemistry, 371 (1989) C31–C34
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20066PC

Preliminary communication

The synthesis, electrochemistry and molecular structure of $[Fe(\eta^5\text{-}C_5H_4S)_2Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}]$

R. Peter Sidebotham, Paul D. Beer, Thomas A. Hamor *, Christopher J. Jones * and Jon A. McCleverty

Department of Chemistry, University of Birmingham, PO Box 363, Birmingham, B15 2TT (U.K.)

(Received March 16th, 1989)

Abstract

The new bimetallic complex $[Fe(\eta^5\text{-}C_5H_4S)_2Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}]$ has been obtained from the reaction between $[Fe(\eta^5\text{-}C_5H_4SH)_2]$ and $[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}I_2]$. Electrochemical studies reveal an anomalously cathodic oxidation potential for the metallocene redox centre. An X-ray diffraction study has revealed an Fe–Mo distance of 4.147(2) Å, with the ferrocenyl moiety oriented towards the nitrosyl ligand on the molybdenum atom (Fe---O 3.976(6) Å), but provides no evidence for an interaction between the iron atom and the molybdenum-bound nitrosyl which might account for the electrochemical findings.

The observation, by Sano et al. [1] that the ^{59}Fe Mössbauer spectra of ferrocenophane derivatives, such as $[Fe(\eta^5\text{-}C_5H_4CH_2)_2](HgCl_2)_3$, contain anomalously large quadrupolar splittings has been rationalised in terms of Fe–Hg interactions. This proposal has stimulated interest in complexes of the type $[Fe(\eta^5\text{-}C_5H_4ER)_2MX_2]$ (ER = SMe, SPr^i, SBu^i, SBz, SPh and M = Pd or Pt with X-Cl or Br; ER = PPh_2 and M = Pd and X = Cl or M = Pt and X = Bu or Cl) [2,3] where Pd or Pt atoms are held in close proximity to the ferrocenyl moiety. However, no evidence for Fe–M interactions was found in these complexes. In contrast, structural studies of the complexes $[Fe(\eta^5\text{-}C_5H_4S)_2M(PPh_3)]$ (M = Pd or Pt) [4,5] have revealed short Fe–M contacts, which are attributed to weak dative bonding between Fe and M [5].

In our laboratory we have been studying [6–9] the effects of redox active transition metal containing substituents, R, on the electrochemical properties of complexes of the type $[Mo(NO)L^{\star}Cl(ZR)]$ ($L^{\star}$ = hydrotris(3,5-dimethylpyrazolyl) borate, Z = O, S, NH). In compounds in which R = *meta*- or *para*-$[C_6H_4ZMo(NO)LCl]$ substantial interactions between the redox active mononitrosylmolybdenum centres may be detected by cyclic voltammetry. We have also examined complexes such as $[M(\eta^5\text{-}C_5H_4CH_2O)_2Mo(NO)L^{\star}]$ (M = Fe, Ru) and $[\{Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}$

0022-328X/89/$03.50

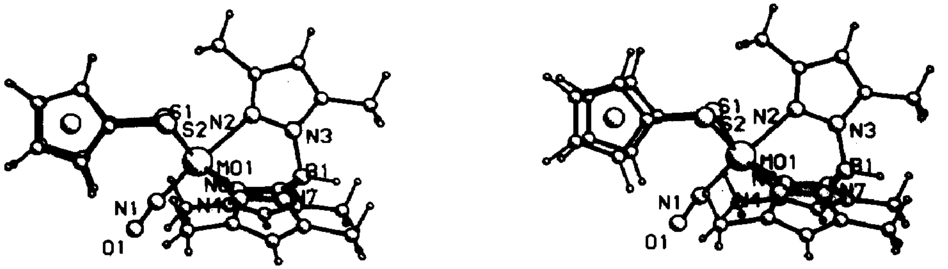

Fig. 1. A Stereoscopic view of the complex in a direction perpendicular to the plane of the lower of the two cyclopentadienyl rings (interplanar angle 3.95°). Selected bond lengths and angles: Fe–C 2.017(7)–2.060(7), mean 2.042 Å, Mo–S, 2.356(2), 2.375(2), Mo–N1 1.838(5), Mo–N2 2.263(4), Mo–N4 2.196(5), Mo–N6 2.202(5), S1–C 1.762(7), S2–C 1.761(7) Å, N1–Mo–N2 176.2(2), S1–Mo–N4 170.7(1), S2–Mo–N6 169.2(1), Mo–S1–C 112.6(2), Mo–S2–C 113.0(2)°.

$C_5H_4CH_2O)\}_2MoL^*]$. [10] Changing M from Fe to Ru in $[M(\eta^5\text{-}C_5H_4CH_2O)_2\text{-}Mo(NO)L^*]$ has no effect on the reduction potential associated with the $\{Mo(NO)\}$ moiety. Similarly, bringing the $\{Mo(NO)\}$ moiety into closer proximity to the ferrocenyl Fe by chelation in $[Fe(\eta^5\text{-}C_5H_4CH_2O)_2Mo(NO)L^*]$, as compared to $[\{Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH_2O)\}_2MoL^*]$, has no significant effect on the ferrocenyl oxidation potential [10]. These observations are in accord with the absence of significant interaction between M and Mo. This is as might be expected in molecules where the CH_2 bridging groups separate the two redox centres in both a spacial and an electronic sense. However, in $[Fe\{(\eta^5\text{-}C_5H_4SMo(NO)L^*Cl\}_2]$ [11] electrochemical measurements indicate that there is an interaction between the two $\{Mo(NO)\}$ centres which is of similar magnitude to that found in $[1,3\text{-}C_6H_4\{SMo(NO)LCl\}_2]$. This interaction is mediated by the 1,1′-dithiaferrocenyl moiety and the ferrocenyl oxidation potential in this complex was 130 mV more anodic than that of $[Fe(\eta^5\text{-}C_5H_4SH)_2]$. Consequently we were interested to determine whether a significantly larger interaction might arise between the $\{Mo(NO)\}$ centre and the ferrocenyl redox centre in molybdenum-containing systems structurally related to $[Fe(\eta^5\text{-}C_5H_4S)_2MPPh_3)]$ (M = Pd or Pt).

The new bimetallic complex $[Fe(\eta^5\text{-}C_5H_4S)_2Mo(NO)L^*]$ has been synthesised from the reaction between the known compounds $[Fe(\eta^5\text{-}C_5H_4SH)_2]$ [12] and $[Mo(NO)L^*I_2]$ [6]. The complex has been fully characterised by infrared, ^1H NMR, ^{13}C NMR and mass spectroscopy as well as by elemental analyses and an X-ray diffraction study. This revealed that the cyclopentadienyl rings of the ferrocenyl moiety are nearly eclipsed, in the solid state at least, as is commonly found (Fig. 1). *Crystal data.* $C_{25}H_{30}BN_7O_{52}FeMo$, $M = 671.3$ monoclinic space group $P2_1/n$, a 10.434(5), b 19.460(7), c 13.792(7) Å, β 92.42(4)°, V 2798 Å^3, $Z = 4$, D_c 1.594 g cm^{-3}, $F(000) = 1368$, $\mu(\text{Mo-}K_\alpha)$ λ 0.71069Å) 11.4 cm^{-1}, 3390 reflections measured on an Enraf–Nonius CAD-4 diffractometer in the range $2 < \theta < 25°$ and having $I > 2.5\sigma(I)$ were used in the analysis. The structure was solved by Patterson and Fourier methods and refined [13–15] by least squares with anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions. The refinement converged (all shifts $< 0, 1\sigma$) with R and R_w 0.044 and 0.054, $w = 1/\sigma^2(F)$ and residual electron density within ± 0.65 Å^{-3}. The atomic coordinates and a complete list of bond lengths and angles have been deposited with the Cambridge Crystallographic data Centre. The Fe–Mo distance is

4.147(2) Å, indicating the absence of any direct interaction between the 18-electron Fe centre and the formally 16-electron Mo centre.

The electrochemical properties of $[Fe(\eta^5\text{-}C_5H_4S)_2Mo(NO)L^\star]$ were investigated by cyclic voltammetry at a Pt bead electrode using dichloromethane solutions containing 0.2 mole dm^{-3} $[NBu_4]BF_4$ as supporting electrolyte. An SCE reference electrode was used in conjunction with 1,1′-diacetylferrocene as an internal standard. The reduction potential of the {Mo(NO)} redox centre was observed at −0.60 V which may be compared with values of −0.64 V for $[Mo(NO)L^\star(SPh)_2]$ and −0.35 V for $[Mo(NO)L^\star(S_2C_6H_3\text{-}3\text{-}Me)]$ [16,17]. The formation of a chelate ring in $[Mo(NO)L^\star(S_2C_6H_3\text{-}3\text{-}Me)]$ produces an anodic shift in reduction potential with respect to that for $[Mo(No)L^\star(SPh)_2]$ because chelation reduces opportunities for $p_\pi \rightarrow d_\pi$ donation from S to Mo [17]. The finding that the reduction potential of $[Fe(\eta^5\text{-}C_5H_4S)_2Mo(NO)L^\star]$ is more cathodic than that of $[Mo(NO)L^\star(S_2C_6H_3\text{-}3\text{-}Me)]$, although more anodic than that of $[Mo(NO)L^\star(S_2C_6H_3\text{-}3\text{-}Me)]$, is in accord with the $[Fe(\eta^5\text{-}C_5H_4S)_2]^{2-}$ ligand's being a better electron donor than $S_2C_6H_3\text{-}3\text{-}Me^{2-}$. This may be rationalised in terms of the putative negative charge on the C_5H_4 ring facilitating electron donation from S to Mo, as compared to the situation with the formally neutral aryl ring in $S_2C_6H_3\text{-}3\text{-}Me^{2-}$.

More difficult to explain is the finding that the oxidation process attributable to the ferrocenyl moiety in $[Fe(\eta^5\text{-}C_5H_4S)_2Mo(NO)L^\star]$ is observed at +0.54 V. This value is more cathodic than those of +0.65 and +0.85 V observed for $[Fe(\eta^5\text{-}C_5H_4SH)_2]$ and $[Fe(\eta^5\text{-}C_5H_4S)_2S]$ respectively. It is also substantially more cathodic than the value of +0.78 V found for $[Fe\{(\eta^5\text{-}C_5H_4S)Mo(NO)ClL^\star\}_2]$ [11]. This finding is contrary to expectations based on the effect of adding an electron withdrawing 16-electron Mo centre to the ferrocenyl redox centre.

One possible explanation for this anomally is that the oxidised form of the complex is stabilised by an interaction between the iron atom and the oxygen atom of the nitrosyl group. The structural study shows that the nitrosyl ligand is in close proximity to the Fe atom in $[Fe(\eta^5\text{-}C_5H_4S)_2Mo(NO)L^\star]$ with an Fe–O distance of 3.976(7) Å. The possibility thus exists that, in $[Fe(\eta^5\text{-}C_5H_4S)_2Mo(NO)L^\star]^+$, the nitrosyl oxygen has the potential to act as a donor towards the iron; the converse of the observed situation in $[Fe(\eta^5\text{-}C_5H_4S)_2Pt(PPh_3)]$[5] where it is the iron which appears to act as a donor. The presence of some Fe–O interaction, even in the neutral complex, might be inferred from the unusually low value of 1634 cm^{-1} for $\nu(NO)$. This may be compared with values of 1685, 1668, 1682 and 1660 cm^{-1} for $[Mo(NO)L^\star Cl(SPh)]$, $[Fe\{(\eta^5\text{-}C_5H_4SMo(NO)L^\star Cl\}_2]$, $[Mo(NO)L^\star(SPh)_2]$ and $[Mo(NO)L^\star(S_2C_6H_3\text{-}3\text{-}Me)]$ respectively [11,16,17].

Despite these spectroscopic findings, from a geometric point of view there is no clear evidence for an Fe–nitrosyl interaction in $[Fe(\eta^5\text{-}C_5H_4S)_2Mo(NO)L^\star]$. Some peculiarities are apparent in the geometry of the Mo–N–O grouping, e.g. the short N–O bond length of 1.123(6) Å, appears to conflict with the spectroscopic results. The long Mo–N bond of 1.838(5) Å is also noteworthy. The Mo–N–O angle of 172.5(5)° lies at the low extreme of the range found for the corresponding angles in the crystal structural of fourteen complexes [18–20] containing the {Mo(NO)L*} moiety. In these cases the angular range is 174.0–179.6° with a mean value of 177.0°. However, the bending of the Mo–N–O grouping here is in such a direction as to actually increase slightly the Fe–O distance as compared to that expected for a linear nitrosyl. The shortest nitrosyl–ferrocenyl interactions involve two short contacts of 2.34 and 2.48 Å between the nitrosyl oxygen atom and hydrogen atoms of the cyclopentadienyl rings.

Further studies are in progress in an attempt to obtain structural, or other definitive evidence which will establish whether a nitrosyl–Fe interaction in $[Fe(\eta^5\text{-}C_5H_4S)_2Mo(NO)L^*]^+$ exists to account for the anomalous metallocene redox potential of this compound.

References

1 M. Watanabe, H. Ichikawa, I. Motoyama and H. Sano, Bull. Chem. Soc. Japan, 56 (1983) 3291.
2 B.M. McCulloch, D.H. Ward, J.D. Woolins and C.H. Brubaker Jr., Organometallics, 4 (1985) 1425.
3 G.M. Whitesides, J.F. Gaasch and E.S. Stedronsky, J. Am. Chem. Soc., 94 (1972) 5258.
4 D. Seyferth, B.W. Hames, T.G. Rucker, M. Cowie and R.S. Dickson, Organometallics, 2 (1983) 2472.
5 S. Akabori, T. Kumagai, T. Shirahige, S. Sato, K. Kawazoe, C. Tamura and M. Sato, Organometallics, 6 (1987) 526.
6 J.A. McCleverty, Chem. Soc. Rev., 12 (1983) 331.
7 S.M. Charsley, C.J. Jones, J.A. McCleverty, B.D. Neaves and S.J. Reynolds, Transition Metal Chem., 11 (1986) 329.
8 S.M. Charsley, C.J. Jones, J.A. McCleverty, B.D. Neaves and S.J. Reynolds and G. Denti, J. Chem. Soc., Dalton Trans., (1988) 293.
9 S.M. Charsley, C.J. Jones, J.A. McCleverty, B.D. Neaves and S.J. Reynolds, J. Chem. Soc., Dalton Trans., (1988) 301.
10 P.D. Beer, C.J. Jones, J.A. McCleverty, and R.P. Sidebotham, J. Organomet. Chem., 325 (1987) C19.
11 P.D. Beer, S.M. Charsley, C.J. Jones and J.A. McCleverty, J. Organomet. Chem., 307 (1986) C19.
12 J.J. Bishop, A. Davison, M.L. Katcher, D.W. Lichtenburg, R.E. Merrill and J.C. Smart, J. Organomet. Chem., 27 (1971) 241.
13 G.M. Sheldrick, SHELX, Program for Crystal structure determination, University of Cambridge, 1976.
14 P. Seiler and J.M. Dunitz, Acta Cryst. B, 38 (1982) 1741.
15 P.D. Beer, C.D. Bush and T.A. Hamor, J. Organomet. Chem., 339 (1988) 133.
16 N. AlObaidi, M. Chaudhury, D. Clague, C.J. Jones, J.C. Pearson, J.A. McCleverty and S.S. Salam, J. Chem. Soc., Dalton Trans., (1987) 1733.
17 N. AlObaidi, C.J. Jones and J.A. McCleverty, Polyhedron, 8 (1989) 1033.
18 N. AlObaidi, T.A. Hamor, C.J. Jones, J.A. McCleverty and K. Paxton, J. Chem. Soc., Dalton Trans., (1986) 1525, and ref. therein.
19 N. AlObaidi, T.A. Hamor, C.J. Jones, J.A. McCleverty and K. Paxton, J. Chem. Soc., Dalton Trans., (1987) 2653.
20 N. AlObaidi, T.A. Hamor, C.J. Jones, J.A. McCleverty, K. Paxton, A.J. Howes and M.B. Hursthouse, Polyhedron, 7 (1988) 1931.