

Electrochemical interactions in binuclear molybdenum and tungsten nitrosyl complexes incorporating saturated *n*-alkanediolate bridging ligands. Crystal structures of $[\text{Mo}(\text{NO})(\text{Tp}^{\text{Me}_2})\text{I}\{\text{O}(\text{CH}_2)_2\text{OCOCH}_3\}]$ and $[\text{W}(\text{NO})(\text{Tp}^{\text{Me}_2})\text{I}_2] \cdot 0.5\text{I}_2 \cdot 0.5\text{C}_6\text{H}_5\text{CH}_3$

Andrzej J. Włodarczyk^{a,*}, Piotr P. Romańczyk^a, Stefan S. Kurek^a,
Wojciech Nitek^b, Jon A. McCleverty^c

^a Faculty of Chemical Engineering and Technology, Cracow University of Technology, 31-155 Kraków, Poland

^b Faculty of Chemistry, Jagiellonian University, ul. Ingardena 3, 30-060 Kraków, Poland

^c School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK

Received 5 September 2007; accepted 12 November 2007

Available online 26 December 2007

Abstract

A series of bimetallic ($[\{\text{M}(\text{NO})(\text{Tp}^{\text{Me}_2})\text{X}\}_2(\text{Q})][\text{Tp}^{\text{Me}_2} = \text{tris}(3,5\text{-dimethylpyrazolyl})\text{borate}; \text{M} = \text{Mo}, \text{X} = \text{Cl}, \text{Q} = \text{O}(\text{CH}_2)_n\text{O}, n = 3, 5, 6, \text{ or } \text{OCH}_2(\text{CF}_2)_3\text{CH}_2\text{O}; \text{M} = \text{Mo}, \text{X} = \text{I}, n = 3 \text{ or } 4; \text{M} = \text{W}, \text{X} = \text{Cl}, n = 3\text{--}6, \text{ or } \text{OCH}_2(\text{CF}_2)_3\text{CH}_2\text{O}; \text{M} = \text{W}, \text{X} = \text{Br}, n = 2]$), and a number of monometallic complexes ($[\text{M}(\text{NO})(\text{Tp}^{\text{Me}_2})\text{X}(\text{QH})][\text{M} = \text{Mo}, \text{X} = \text{Cl}, \text{Q} = \text{O}(\text{CH}_2)_n\text{O}, n = 3, \text{ or } \text{OCH}_2(\text{CF}_2)_3\text{CH}_2\text{O}; \text{M} = \text{W}, \text{X} = \text{Br}, n = 2]$) were prepared. The heterobimetallic complex $[\{\text{Mo}(\text{NO})(\text{Tp}^{\text{Me}_2})\text{Br}\}\text{O}(\text{CH}_2)_2\text{O}\{\text{W}(\text{NO})(\text{Tp}^{\text{Me}_2})\text{Br}\}]$ was also obtained. All compounds were characterised by elemental and mass analyses, ¹H NMR and IR spectroscopy. Electrochemical studies (CV and DPV) of the bimetallic species reveal that the metal–metal interactions decrease by *ca.* 100 mV per CH₂ group with increased length for C₂ to C₄ bridges and become undetectable for complexes with bridges longer than C₄. The substitution of fluorine into the C₅ bridge causes the effect to become measurable due to easier polarisation of the σ-bond framework. The crystal structures of $[\text{Mo}(\text{NO})(\text{Tp}^{\text{Me}_2})\text{I}\{\text{O}(\text{CH}_2)_2\text{OCOCH}_3\}]$ and $[\text{W}(\text{NO})(\text{Tp}^{\text{Me}_2})\text{I}_2] \cdot 0.5\text{I}_2 \cdot 0.5\text{C}_6\text{H}_5\text{CH}_3$ were determined.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Molybdenum nitrosyl complex; Tungsten nitrosyl complex; Bimetallic complexes; Tris(pyrazolyl)borato complexes; Saturated bridging systems; Electrochemical interactions

1. Introduction

The design and synthesis of redox active binuclear complexes in which metal centres are linked *via* bridging ligands enabling electronic interactions between them are of major interest in the development of models for intramolecular electron transfer over long distances, important for under-

standing key processes in both chemistry and biology [1–3]. A significant obvious indication of metal–metal interactions is the separation between redox potentials of two redox centres, $\Delta E_{1/2}$, which depends on the metal, its environment, the length and the geometry of the bridge and its electronic properties. The above interactions may be coulombic through-space and through-bond (π -mesomeric effect, σ -inductive effect) in character.

Numerous examples of bimetallic complexes $\{\text{M}(\text{NO})(\text{Tp}^{\text{Me}_2})\text{X}\}^{+/0}$ [$\text{Tp}^{\text{Me}_2} = \text{HB}(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_3$, X = halide]

* Corresponding author. Tel./fax: +48 126325371.

E-mail address: awlodar@pk.edu.pl (A.J. Włodarczyk).

with π -acceptor ligands (e.g. aromatic heterocycles, polyenes) that make the delocalisation of the unpaired electron possible have been reported in the literature. The highest values of $\Delta E_{1/2}$ were obtained for complexes in which $Q = \text{pyrazine}$ (1440 mV, $K_c = 2.2 \times 10^{24}$) [4], $Q = 1,4\text{-HNC}_6\text{H}_4\text{NH}$ (920 mV) [5], $Q = 4,4'\text{-bipy}$ (765 mV) [6], $Q = \text{OC}_6\text{H}_4(2,5\text{-C}_4\text{H}_2\text{S})_2\text{C}_6\text{H}_4\text{O}$ (670 mV) [7], and $Q = \text{pyC}\equiv\text{Cpy}$ (560 mV) [8]. In all these examples, electrochemical interactions were apparently much greater than in the Creutz-Taube ion (390 mV) [9], although the latter measurements were obtained in aqueous conditions, whereas the former were measured in dichloromethane, solvent effects often having a significant influence on $\Delta E_{1/2}$. It is worth mentioning that observable electrochemical interactions and significant magnetic interactions were detected in the complex $[\{\text{Mo}(\text{NO})(\text{Tp}^{\text{Me}_2})\text{Cl}\}_2\{4,4'\text{-NC}_5\text{H}_4\text{-}(\text{CH}=\text{CH})_4\text{C}_5\text{H}_4\text{N}\}]$, in which the $\text{Mo}\cdots\text{Mo}$ distance is *ca.* 2 nm [10]. The introduction of a saturated section into the bridge, as, e.g. in $Q = 1,2\text{-bi}(4\text{-pyridyl})\text{ethane}$ (105 mV) [6], considerably decreases $\Delta E_{1/2}$, but does not exclude electronic and magnetic through-bridge interactions. Electron tunnelling was shown as possible for $\{\text{Ru}(\text{NH}_3)_5\}^{n+}$ complexes having fully saturated bridging ligands based on a rigid spirane system with the $\text{Ru}\cdots\text{Ru}$ distance as long as 17.5 Å [11]. Self-arranged monolayers of alkanethiols adsorbed on gold electrodes are also used in the study of electron transfer through the saturated hydrocarbon chains [12]. Merely a few examples of $\{\text{M}(\text{NO})(\text{Tp}^{\text{Me}_2})\text{X}\}^+$ complexes containing completely saturated bridges have been described in the literature, among them with $Q = \text{NH}(\text{CH}_2)_n\text{NH}$ ($n = 2, 3$) [13], $Q = \text{NC}_4\text{H}_8\text{N}$ (560 mV) [14] and $Q = \text{O}(\text{CH}_2)_4\text{O}$ (100 mV) [15]. The first one shows irreversible reduction processes, because of the presence of N–H protons, which excludes a detailed discussion of metal–metal interactions in these systems, whereas for the species with a cyclic piperazine bridge, the $\Delta E_{1/2}$ value should be treated with caution because of the irreversibility of the second reduction potential.

We showed in our previous paper [16] that despite the presence of a saturated bridge the complexes $[\{\text{Mo}(\text{NO})(\text{Tp}^{\text{Me}_2})\text{X}\}_2\{\text{O}(\text{CH}_2)_2\text{O}\}]$ ($X = \text{Cl}$ or Br) exhibit two chemically reversible one-electron reduction processes separated by a potential difference, $\Delta E_{1/2}$, of *ca.* 310 mV, demonstrating thus significant electrochemical interactions comparable to their analogue with the 1,2- $\text{O}_2\text{C}_6\text{H}_{10}$ cyclic bridge ($\Delta E_{1/2}$ 300 mV) [17], and $\{\text{Mo}(\text{NO})(\text{Tp}^{\text{Me}_2})\text{Cl}\}^{+/0}$ complexes with aromatic bridges, in which mesomeric effects are not possible, e.g. 1,3- $\text{O}_2\text{C}_6\text{H}_4$ ($\Delta E_{1/2}$ 260 mV) [18], 1,3- $(\text{HN})_2\text{C}_6\text{H}_4$ ($\Delta E_{1/2}$ 370 mV) [19].

In order to determine the magnitude and the range of electrochemical interactions in the molybdenum and tungsten nitrosyls containing *n*-alkanediolate bridging ligands we synthesised a series of complexes with increasing alkyl chain length. The effect of modifying the electronic properties of the alkyl bridge by introducing fluorine atoms into it was also investigated.

2. Results and discussion

2.1. Synthetic and spectroscopic studies

The reactions between $[\text{M}(\text{NO})(\text{Tp}^{\text{Me}_2})\text{X}_2]$ and the appropriate α,ω -diol afforded mixtures of mono- and bimetallic complexes which are air-stable and the majority of which may be separated by column chromatography on silica gel using CH_2Cl_2 as eluant. When passing the monometallic complexes through the chromatographic column repeatedly, bimetallic complexes were always formed. Bimetallic species were also formed as a result of heating $[\text{Mo}(\text{NO})(\text{Tp}^{\text{Me}_2})\text{Cl}\{\text{O}(\text{CH}_2)_n\text{OH}\}]$ with acetic acid (*ca.* 0.1 M) in dichloromethane.

The monometallic complex, $[\text{Mo}(\text{NO})(\text{Tp}^{\text{Me}_2})\text{Cl}\{\text{O}(\text{CH}_2)_3\text{OH}\}]$ (**18**), could not be isolated in its pure form. Every attempt to isolate it resulted in a mixture of the monometallic in a great excess and corresponding bimetallic complex.¹ A minor product isolated as green crystals from the reaction between $[\text{Mo}(\text{NO})(\text{Tp}^{\text{Me}_2})\text{I}_2]$ and ethane-1,2-diol in dichloromethane in the presence of silver acetate, was confirmed by X-ray crystallography to be 2-acetoxyethanolate complex **6**. Despite the large number of syntheses of this type of complex described in the literature such a by-product has never been reported. Generally, acetoxy complexes are intermediate products, that easily undergo substitution by alkoxy ligands because of the labile character of acetoxy group [22]. The compounds obtained from the reaction between **17** and ethane-1,2-diol decomposed during column chromatography.

The reaction between $[\text{Mo}(\text{NO})(\text{Tp}^{\text{Me}_2})\text{Br}\{\text{OCH}_2\text{-CH}_2\text{OH}\}]$ and $[\text{W}(\text{NO})(\text{Tp}^{\text{Me}_2})\text{Br}_2]$ afforded the heterobimetallic complex. The ¹H NMR spectrum of this compound indicated it to be a mixture of two different diastereoisomers which could not be separated by column chromatography.

As can be seen from Table 1, all new compounds gave satisfactory elemental analyses, and mass spectrometry usually provided parent molecular ions (M^+) in addition to fragment ions consistent with the loss of halide and/or NO.

The infrared spectra of all the complexes exhibited bands typical for $\text{HB}(\text{Me}_2\text{pz})_3^-$: $\nu(\text{BH})$ at *ca.* 2550 cm^{-1} , $\nu(\text{C-Me})$ in the range of 1366–1451 cm^{-1} and $\nu(\text{C}=\text{C})$ at *ca.* 1540 cm^{-1} . The stretching frequency of the nitrosyl group appeared as the most intense, sharp peak, which reflected the fact that the force constant is related to the effective nuclear charge on the metal centre, which in turn depends on the electron properties of co-ligands X, Y. Mono- and bimetallics showed a single $\nu(\text{N}=\text{O})$ in the

¹ The ¹H NMR spectrum of **18** was deduced from the data of the mixture by subtracting the data of the bimetallic in purity: $\delta_{\text{H}}(\text{CHCl}_3)$ 5.91, 5.86, 5.76 (1H, s; 1H, s; 1H, s; $\text{Me}_2\text{C}_3\text{HN}_2$); 2.51, 2.45, 2.38, 2.37, 2.35, 2.34 (3H, s; 3H, s; 3H, s; 3H, s; 3H, s; 3H, s; $(\text{CH}_3)_2\text{C}_3\text{HN}_2$); 6.10, 5.96 (1H, m; 1H, m; $\text{OCH}_2\text{CH}_2\text{CH}_2\text{OH}$); 3.88 (2H, m; $\text{OCH}_2\text{CH}_2\text{-CH}_2\text{OH}$); 2.20 (2H, m; $\text{OCH}_2\text{CH}_2\text{CH}_2\text{OH}$).

Download English Version:

<https://daneshyari.com/en/article/1339663>

Download Persian Version:

<https://daneshyari.com/article/1339663>

[Daneshyari.com](https://daneshyari.com)