

## NITROSYL TRIS(3,5-DIMETHYLPYRAZOLYL)BORATO COMPLEXES OF MOLYBDENUM BINDING PYRIDINE LIGANDS WITH ELECTRON-WITHDRAWING GROUPS AT THE 3-POSITION

Keira STOBIE<sup>1</sup>, Zoe R. BELL<sup>2</sup> (née REEVES), Michael D. WARD<sup>3,\*</sup>  
and Jon A. McCLEVERTY<sup>4,\*</sup>

*School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, U.K.;*  
*e-mail:* <sup>1</sup> keira.stobie@bristol.ac.uk, <sup>2</sup> zoe.bell@bristol.ac.uk, <sup>3</sup> mike.ward@bristol.ac.uk,  
<sup>4</sup> jon.mccleverty@bristol.ac.uk

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*Dedicated to the memory of the late Professor A. A. Vlček: Tony to his British friends – an enthusiast for coordination chemistry, a professional electrochemist, and a great survivor.*

The octahedral nitrosyl complexes [MoCl(NO)(3-PhCH=CHCOpy)(Tp<sup>Me,Me</sup>)] and [MoCl(NO){3,5-(MeCO)<sub>2</sub>py}(Tp<sup>Me,Me</sup>)] (py = pyridyl) were synthesized and characterized spectroscopically. Both complexes underwent reduction and oxidation giving anionic and cationic species, respectively. Both complexes were also characterized by X-ray crystallography that confirmed their essential octahedral geometry and showed that the Mo–NO bond distance reflected the acceptor ability of the pyridine ligands.

**Keywords:** Nitrosyl; Molybdenum; Pyridines; Redox-activity; X-Ray diffraction; Cyclic voltammetry; Electrochemistry.

Compounds that absorb very strongly in the near-infrared (NIR) region of the electromagnetic spectrum (900–2 000 nm), may be of use in a variety of applications, including optical data storage media based on NIR lasers, dyes for Q-switching of lasers (converting a continuous low-energy laser into very short high-energy pulses), and optical limiters for use as protection devices against high-intensity radiation damage<sup>1</sup>. Electrochromic materials, that is substances which change their “colour” on application of a potential (usually requiring a change in oxidation level of the material), have also attracted great interest because of their potential for applications in, for example, “smart” window and information display and storage devices<sup>2</sup>. The syntheses of compounds capable of strong electrochromism in the NIR region are therefore an important and challenging objective in contemporary molecular opto-electronics.

Recently we have found two categories of molybdenum complexes that are capable of generating exceptionally strong and switchable optical absorbance in the NIR region. These are based on (i) dinuclear oxomolybdenum(V) tris(3,5-dimethylpyrazolyl)borate ( $\text{Tp}^{\text{Me,Me}}$ ) species in which the two  $\text{Mo}(\text{O})^{3+}$  fragments are linked by bis(phenolate) bridges<sup>3</sup>, and (ii) mononuclear nitrosyl molybdenum(II)  $\text{Tp}^{\text{Me,Me}}$  complexes containing pyridine ligands bearing electron-withdrawing groups, *e.g.* COMe, COPh or CN, at the 3-position<sup>4</sup>. The former group exhibits strong absorptions in the range of 1 000–1 600 nm on (reversible) *oxidation*, and the latter, *viz.*  $[\text{MoCl}(\text{NO})(3\text{-Rpy})(\text{Tp}^{\text{Me,Me}})]$ , show similar such absorptions on (reversible) *reduction*; molar absorption coefficients can be up to *ca* 60 000  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ .

While developments involving oxomolybdenum(V) complexes that undergo the “on/off” process for several thousand cycles, are described elsewhere<sup>5</sup>, we have also attempted to optimize the electrochromic NIR response of the pyridine complexes. This could be done either by extending the delocalization of the acceptor group at position 3, or by having two acceptor groups at the *meta* positions, as in 3-(PhCH=CHCO)py, **1**, or 3,5-(MeCO)<sub>2</sub>py, **2** (Fig. 1), respectively.

## EXPERIMENTAL

### General

The molybdenum precursor  $\text{HEt}_3\text{N}[\text{MoCl}_2(\text{NO})(\text{Tp}^{\text{Me,Me}})]$  was prepared as described<sup>6</sup> previously; the ligands **1** and **2** were also prepared according to published methods<sup>7,8</sup>. Other starting materials were purchased from Aldrich or Lancaster and used as received. Solvents were dried before use, and all reactions were carried out under  $\text{N}_2$ . Purification by column chromatography was performed using silica gel (70–230 mesh) with eluents as detailed in the relevant syntheses. Elemental analyses were performed by the Microanalytical laboratory at the University of Bristol.

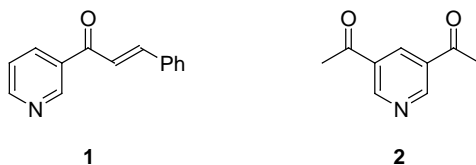


FIG. 1

Structural formulae of ligands **1** and **2**

FAB (fast atom bombardment) and EI (electron impact) mass spectra were recorded using a VG-Autospec instrument.  $^1\text{H}$  NMR spectra were measured in  $\text{CDCl}_3$  using a Jeol Lambda 300 spectrometer, and EPR measurements were made in  $\text{CH}_2\text{Cl}_2$  solution at room temperature, using a Bruker ESP-300E spectrometer. IR spectra (KBr discs) and UV-VIS spectra ( $\text{CH}_2\text{Cl}_2$ ) were recorded using Perkin-Elmer FT-1600 spectrometer and Lambda 2 spectrophotometer, respectively. Electrochemical measurements were carried out using a PC-controlled EG&G PAR Model 273A potentiostat, with Pt-bead working and counter electrodes and a Ag wire electrode as a pseudoreference, in  $\text{CH}_2\text{Cl}_2$  (*ca*  $10^{-3}$  mol  $\text{dm}^{-3}$  in complex) containing  $\text{Bu}_4\text{NPF}_6$  or  $\text{Bu}_4\text{NBF}_4$  as supporting electrolytes ( $1 \cdot 10^{-1}$  mol  $\text{dm}^{-3}$ ). Ferrocene was added as an internal standard, and all potentials are quoted relative to the ferrocene/ferrocenium couple ( $\text{Fc}/\text{Fc}^+$ ).

#### Synthesis of $[\text{MoCl}(\text{NO})\{3\text{-(PhCH=CHCO)py}\}(\text{Tp}^{\text{Me,Me}})]$ (**3**)

To a pale yellow solution of **1** (0.3 g, 1.4 mmol) in dry toluene (100  $\text{cm}^3$ )  $[\text{MoCl}_2(\text{NO})(\text{Tp}^{\text{Me,Me}})]$  (0.9 g, 1.9 mmol) and  $\text{Et}_3\text{N}$  (anhydrous, *ca* 2  $\text{cm}^3$ ) were added, the brown mixture was refluxed (6 h), allowed to cool to room temperature and stirred overnight. The dark green solution was evaporated *in vacuo* giving a dark brown paste which was dissolved in the minimum volume of  $\text{CH}_2\text{Cl}_2$  and chromatographed using  $\text{CH}_2\text{Cl}_2$  as eluant. The third fraction was collected and the solvent removed *in vacuo*, to give a dark red-brown solid (0.18 g, 19%). This was further purified by column chromatography (0.5% THF/dichloromethane) to remove a decomposition product (final yield 0.12 g, 13%). FAB MS,  $m/z$ : 669 [ $\text{M}^+$ ]. IR (KBr): 2 546 ( $\nu_{\text{BH}}$ ), 1 669 ( $\nu_{\text{CO}}$ ), 1 624 ( $\nu_{\text{NO}}$ )  $\text{cm}^{-1}$ . UV-VIS ( $\text{CH}_2\text{Cl}_2$ ),  $\lambda_{\text{max}}$  ( $\epsilon_{\text{max}}$ ): 280 (13.7), 320 (20.6), 413 (sh), 510 (sh) nm ( $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1} \cdot 10^{-3}$ ). EPR ( $\text{CH}_2\text{Cl}_2$ ):  $g_{\text{iso}} = 1.979$  ( $A_{\text{Mo}} = 48.9$  G). For  $\text{C}_{29}\text{H}_{33}\text{BClMoN}_8\text{O}_2$  (667.8) calculated: 52.2% C, 4.8% H, 16.2% N; found: 52.0% C, 4.9% H, 15.7% N.

#### Synthesis of $[\text{MoCl}(\text{NO})\{3,5\text{-(MeCO)}_2\text{py}\}(\text{Tp}^{\text{Me,Me}})]$ (**4**)

To a suspension of  $\text{HEt}_3\text{N}[\text{MoCl}_2(\text{NO})(\text{Tp}^{\text{Me,Me}})]$  (0.54 g, 0.9 mmol) in dry toluene (150  $\text{cm}^3$ ) was added an excess of **2** (0.5 g) and the mixture was refluxed for 3 days. The solvent was evaporated *in vacuo*, leaving a green-black paste which was purified by column chromatography (graduated eluent of 0.7–1.5% THF/ $\text{CH}_2\text{Cl}_2$ ) to give a purple-red solid. The latter was further purified by column chromatography (1% THF/ $\text{CH}_2\text{Cl}_2$ ) to afford the complex as a red-brown solid (0.03 g, 5%). FAB MS,  $m/z$ : 623 [ $\text{M}^+$ ]. IR (KBr): 2 553 ( $\nu_{\text{BH}}$ ), 1 700 ( $\nu_{\text{CO}}$ ), 1 617 ( $\nu_{\text{NO}}$ )  $\text{cm}^{-1}$ . UV-VIS ( $\text{CH}_2\text{Cl}_2$ ),  $\lambda_{\text{max}}$  ( $\epsilon_{\text{max}}$ ): 279 (8.3), 310 (sh), 421 (sh), 539 (0.9) nm ( $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1} \cdot 10^{-3}$ ). EPR ( $\text{CH}_2\text{Cl}_2$ ):  $g_{\text{iso}} = 1.978$  ( $A_{\text{Mo}} = 48.7$  G). For  $\text{C}_{24}\text{H}_{31}\text{BClMoN}_8\text{O}_3 \cdot \text{C}_4\text{H}_8\text{O}$  (621.8) calculated: 48.5% C, 5.7% H, 16.2% N; found: 47.3% C, 6.0% H, 15.5% N.

#### Crystallographic Studies

Crystals of **3** and **4** were grown from  $\text{CH}_2\text{Cl}_2$ /pentane as rectangular prisms. Diffraction intensity data were collected on a Siemens SMART-CCD diffractometer. The software used was SHELXS97 for structure solution<sup>9a</sup>, SHELXL97 for structure refinement<sup>9b</sup>, and SADABS for the absorption correction<sup>10</sup>. Details of the crystal parameters, data collection and refinement are collected in Table I. Neither determination presented any significant problems. Crystallographic data for the structures reported in this paper have been deposited with the Cam-

bridge Crystallographic Data Centre as supplementary publication numbers CCDC-152928 and CCDC-152929. Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

## RESULTS AND DISCUSSION

The complexes were prepared by reaction of either  $[\text{MoCl}_2(\text{NO})(\text{Tp}^{\text{Me,Me}})]$  and the ligand **1** (Fig. 1) with  $\text{Et}_3\text{N}$  as reducing agent which generates substitution-labile  $[\text{MoCl}_2(\text{NO})(\text{Tp}^{\text{Me,Me}})]^-$  *in situ*, or of preformed  $\text{HEt}_3\text{N}[\text{MoCl}_2(\text{NO})(\text{Tp}^{\text{Me,Me}})]$  with **2** (Fig. 1) in toluene. The formation of **3** was relatively straightforward, but in order to produce pure **4**, it was neces-

TABLE I  
Crystal and structure refinement data for **3** and **4**<sup>a</sup>

Parameter	<b>3</b>	<b>4</b>
Empirical formula	$\text{C}_{29}\text{H}_{33}\text{BClMoN}_8\text{O}_2$	$\text{C}_{24}\text{H}_{31}\text{BClMoN}_8\text{O}_3$
$M_w$	667.83	621.77
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
$a$ , Å	10.4294(14)	8.215(4)
$b$ , Å	15.847(2)	19.444(6)
$c$ , Å	18.9798(19)	17.585(6)
$\beta$ , °	98.593(16)	100.11(4)
$V$ , Å <sup>3</sup>	3 101.7(7)	2 765.5(18)
$D_c$ , g cm <sup>-3</sup>	1.430	1.493
Crystal size, mm	0.5 × 0.5 × 0.45	0.4 × 0.3 × 0.2
$Z$	4	4
$\mu$ , mm <sup>-1</sup>	0.549	0.612
Reflections collected:		
total, independent, $R_{\text{int}}$	26 458, 5 474, 0.0405	14 910, 4 862, 0.0568
Final $R1$ , $wR2$ <sup>b,c</sup>	0.0400, 0.1135	0.0422, 0.1017
Largest peak/hole, e Å <sup>-3</sup>	+0.669, -0.646	+0.745, -0.691

<sup>a</sup> Details in common: diffractometer Siemens SMART, using MoK $\alpha$  radiation (0.71073 Å); temperature of data collection, 173 K. <sup>b</sup> Structure was refined on  $F_o^2$  using all data; the value of  $R1$  is given for comparison with older refinements based on  $F_o$  with a typical threshold of  $F \cdot 4\sigma(F)$ . <sup>c</sup>  $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$ , where  $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$  and  $P = [\max(F_o^2, 0) + 2F_c^2]/3$ .

sary to pre-form the reduced molybdenum nitrosyl precursor, as  $\text{HEt}_3\text{N}[\text{MoCl}_2(\text{NO})(\text{Tp}^{\text{Me,Me}})]$ .

The purity and authenticity of the complexes were confirmed by spectroscopic and crystallographic methods. The IR spectra showed absorptions at *ca*  $1\,620\text{ cm}^{-1}$ , typical of this class of 17-valence electron molybdenum nitrosyl complexes, as well as C=O vibrations at  $1\,669$  (**3**) and  $1\,700\text{ cm}^{-1}$  (**4**), as well as bands typical of coordinated  $\text{Tp}^{\text{Me,Me}}$ . The electronic absorption spectra are also characteristic of this group of nitrosyl species, the absorptions at  $510\text{ nm}$  (**3**) and  $539\text{ nm}$  (**4**) being assigned as MLCT transitions involving the pyridine ligands. The complexes are also paramagnetic, their EPR spectra again being characteristic of one unpaired electron at a single  $\text{Mo}(\text{NO})^{2+}$  centre, as we have described<sup>11</sup> previously:  $g_{\text{iso}} = 1.979(1)$  and  $A_{\text{Mo}} = 50(2)\text{ G}$ .

The crystal structures of the complexes are shown in Figs 2 and 3. Both **3** and **4** have the expected pseudo-octahedral geometry around the central metal atom, with the bond lengths and angles comparable to each other and to those reported for similar complexes<sup>4,12</sup>. The electron-withdrawing substituents on the pyridine ligand in each case have noticeable consequences on some of the bond lengths. The more electron density there is at the metal centre, the more back-bonding there will be to the  $\sigma$ -acceptor nitrosyl ligand, which will be manifested in short Mo–NO and long N–O

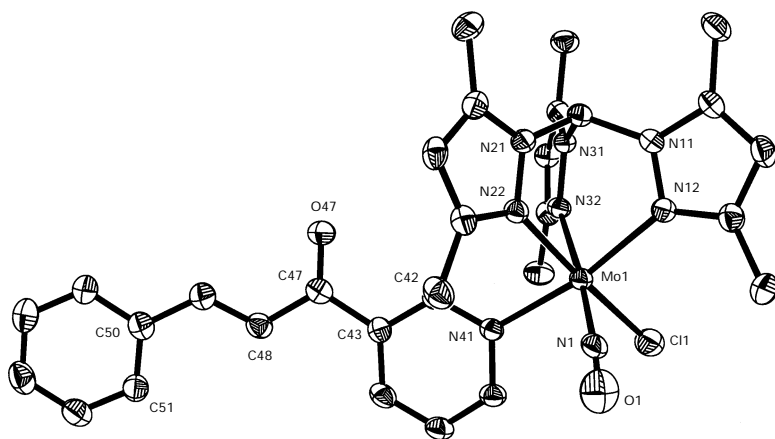


FIG. 2

Crystal structure of complex **3**. Relevant bond distances (in Å): Mo(1)–Cl(1), 2.4555(11); Mo(1)–N(1), 1.868(4); Mo(1)–N(41), 2.192(3); Mo(1)–N(12), 2.162(3); Mo(1)–N(22), 2.165(3); Mo(1)–N(32), 2.257(3); N(1)–O(1), 1.050(4)

separations. Comparison of the bond distances in these two structures with each other and with other structures having the same core, shows this pattern quite clearly. In **4** the N–O distance [0.903(6) Å] is much shorter than in **3** [1.050(4) Å]; in agreement with this, the Mo–NO distance is much longer, at 1.929(6) Å in **4** vs 1.868(4) Å in **3**. This effect means that there is less Mo→NO  $\sigma$ -back-bonding in **4**, consistent with the fact that the pyridine ligand **2** has *two* electron-withdrawing substituents which will reduce the electron density at the metal centre compared to the case with **1** (complex **3**). A similar correlation of the Mo–NO and N–O separations with the electron-withdrawing or electron-releasing nature of the substituents of the pyridine ring exists for other members of the series<sup>4,12</sup>. Interestingly, the Mo–N(pyridyl) and Mo–Cl distances are not so obviously affected and do not simply correlate with the nature of the substituent on the pyridyl ring.

These neutral 17-electron nitrosyl complexes are redox-active, generally undergoing a one-electron oxidation to the 16-electron monocation, and a one-electron reduction to the 18-electron monoanion, *i.e.* the species [MoX(NO)(Rpy)(Tp<sup>Me,Me</sup>)]<sup>n</sup> (X = halide; n = -1, 0, +1) are all accessible. Both

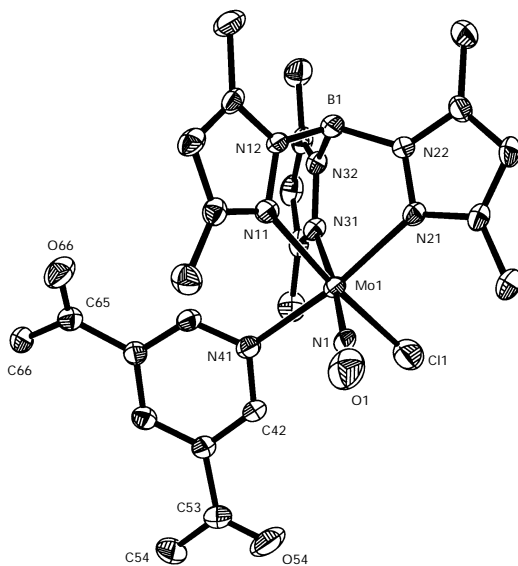


FIG. 3

Crystal structure of complex **4**. Relevant bond distances (in Å): Mo(1)–Cl(1), 2.4448(18); Mo(1)–N(1), 1.929(6); Mo(1)–N(41), 2.207(3); Mo(1)–N(11), 2.185(3); Mo(1)–N(21), 2.154(3); Mo(1)–N(31), 2.231(4); N(1)–O(1), 0.903(6)

the monoanion and monocation can be characterized by spectroelectrochemical techniques, as we have reported<sup>4</sup>, and it was using this technique that we discovered that the monoanions containing R = 3-MeCO, 3-PhCO and 3-CN exhibited strong MLCT absorptions in the range 1 000–1 500 nm. Success with this technique depends on the electrochemical and chemical reversibility of the electron transfer process being observed.

Both **3** and **4** were examined by cyclic and square-wave voltammetry in CH<sub>2</sub>Cl<sub>2</sub> and THF, and both showed that anionic and cationic species could be generated. However, the electrode processes for the formation of what we believe to be [3]<sup>-</sup> and [4]<sup>-</sup> were chemically irreversible,  $E_f = -1.70$  and  $-1.67$  V vs Fc/Fc<sup>+</sup>, respectively. Formation of [3]<sup>+</sup> and [4]<sup>+</sup> was electrochemically quasi-reversible,  $E_f = +0.12$  V ( $\Delta E_p = 90$  mV) and  $+0.15$  V ( $\Delta E_p = 90$  mV), respectively. This is the first time that we have found the reduction of complexes of this type to the 18-electron monoanion to be completely irreversible. It is possible that the electron-withdrawing substituents on the ligands render the pyridyl ligands reducible, such that the reduction has some ligand-centred character: the ground state of the reduced species would therefore have a significant contribution from a canonical form in which there is a pyridyl-based radical, which would provide a facile decomposition pathway. We have no electrochemical evidence to substantiate this view, although the ideas are consistent with data obtained from other related complexes<sup>4,12</sup>.

## CONCLUSIONS

We have prepared two complexes [MoCl(NO){3-(PhCH=CHCO)py}(Tp<sup>Me,Me</sup>)] and [MoCl(NO){3,5-(MeCO)<sub>2</sub>py}(Tp<sup>Me,Me</sup>)] in order to investigate their spectroelectrochemical behaviour on reversible reduction to monoanions. It was expected that the monoanions would exhibit substantial NIR charge-transfer absorption in the region 1 000–1 600 nm, but in the event the reduction processes proved disappointingly and unexpected irreversible. The structures of the two complexes were determined by X-ray crystallography, and showed some interesting correlations of the Mo–NO and N–O distances with the substituents on the pyridyl ring.

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