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Synthesis and Reactivity of a Bio-inspired Dithiolene ligand and its Mo-oxo complex

Jean-Philippe Porcher,[a] Thibault Fogeron,[b] Maria Gomez-Mingot,[c] Lise-Marie Chamoreau,[a] Yun Li*[a] and Marc Fontecave*[a]

Abstract: An original synthesis of the fused pyrano-quinoxaline dithiolene ligand, qpdt2-, is discussed in detail. Specially, the most intriguing step was the introduction of the dithiolene function by the Pd-catalyzed carbon-sulfur coupling reaction. The corresponding Mo=O complex (Bu4N)[MoO(qpdt)2] (2) enjoyed reversible protonation in a strong acidic medium and remained stable under anaerobic conditions. Besides, 2 was found to be very sensitive towards oxygen forming a planar dithiin derivative. Moreover, the qpdt2- ligand in the presence of [MoCl4(BuNC)2] formed an original tetracyclic structure. The products obtained from the unique reactivity of qpdt2- have been characterized by X-ray diffraction, mass spectrometry, NMR spectroscopy, UV-Vis spectroscopy and electrochemistry. The plausible mechanisms for the formation of these products are also enclosed.

Introduction

Six families of Mo or W containing enzymes (oxidoreductases, hydrolases, etc...) have been discovered and characterized structurally by X-ray diffraction methods so far.[2] In general a single Mo/W ion is coordinated by molybdopterin (MPT, Figure 1), which is an unstable fused pyranopterin system containing a dithiolene chelate. During the catalytic cycle, the oxidation number of Mo/W varies from +4 to +6, while the MPT structure remains unchanged.

Several bioinorganic groups have focused their efforts on synthesizing Mo/W-dithiolene complexes as structural and functional analogues of these active sites. The pioneer work was launched by Holm’s group[3] over 20 years ago and was followed by others.[4] We here report the synthesis of a new fused pyrano-quinoxaline dithiolene ligand, qpdt2-, under its protected form 1 (Figure 1). To our knowledge, only very few examples of such dithiolene ligands have been reported so far. Recently, Basu et al. have developed the synthesis of an analogue of 1 and used it as a specific probe for Pb2+ detection.[5] However, this synthetic route required several delicate steps with moderate yields, especially for the pyran ring closure step. No Mo/W complex was reported in their work. Garner and co-workers have synthesized a tricyclic pyranopterin dithiolene ligand system (including the pyrimidine ring).[6] But they failed to complex a Mo/W ion. A Co complex was isolated and characterized instead. Burgmayer’s group have reported the synthesis of the MoV/MoV complexes Tp*MoO(pyrano-S2BMOPP), where Tp* is tris(3,5-dimethylpyrazolyl)hydroborate and “pyrano-S2BMOPP” is a tricyclic pyranopterin dithiolene chelate. The pyran ring is formed through a solvent-dependent spontaneous cyclization.[7]

In a previous communication we have shown that qpdt2- can be used to synthesize a Mo=O complex (Bu4N)[MoO(qpdt)]2 (2, Figure 2). This complex acts as a remarkable catalyst for electro- and photo- reduction of protons into H2 in organic solvents.[8] In the current study, we describe reactions of this complex in the presence of protons and oxygen. Finally, the reactivity of the dithiolene towards [MoCl4(BuNC)2] is also reported. All these reactions illustrate the unique chemical reactivity of this original biomimetic complex.

Results and Discussion

1. Synthesis of the ligand

As regards the synthetic strategy, it seems that the great difficulty resides in the pyran ring closure step.[9] To circumvent this problem, we chose to first prepare the tricyclic skeleton, and to introduce the dithiolene function in a second stage. For this purpose, the bromo-enol 3 was synthesized. 2,3-dichloroquinoxaline (4), underwent a Sonogashira coupling followed by a pyran ring closure step with sodium methylene to afford methyl enol-ether 6, according to a reported procedure.[11] After hydrolysis of 6 under acidic conditions, controlled monobromination of 7 at low temperature afforded 3 in 89 % yield (Scheme 1).
In order to prepare the dithiocarbonate 8 as a protected dithiolen ligand, compound 3 was first treated with O-iso-propylyxanthic acid potassium salt, a classical method for introducing a dithiocarbonate from an α-bromoketone.\(^\text{(10)}\) Despite many attempts under different experimental conditions (reaction temperatures, solvents...), no nucleophilic substitution product was obtained. Only the starting compound 3 was detectable by \(^1\)H NMR spectroscopy. The same results were obtained even when the iodo-enol 9 was employed as the starting reagent. It is likely that, in both 3 and 9, the keto-enol equilibrium is strongly displaced towards the enol form, according to the \(^1\)H NMR data (\(\delta_{\text{H}} = 8.42\) ppm, 1H for 3 and \(\delta_{\text{H}} = 8.47\) ppm, 1H for 9, D$_2$O exchangeable for both protons) and therefore the substitution reaction by a S-nucleophile is disfavored.

Itoh \textit{et al.} have developed a general carbon-sulfur bond formation method via a palladium-catalyzed coupling reaction of aryl bromides/triflates and thiol.\(^\text{(11)}\) In order to insert a thiol surrogate, we extended this methodology to the vinyl bromide function in 3. Thiocetic acid and iso-octyl-3-mercaptopyrrolic acid were tested (Scheme 2). The dimerization product 10 was obtained in both cases. This result strongly suggests that a de-protection step assisted by the adjacent enolate occurred after thiol insertion, resulting in a highly nucleophile thiocene intermediate 11 (Scheme 2). However, what is remarkable is that a protected thiol could indeed replace a vinyl bromide under this condition.

We decided next to prepare the corresponding bromo-vinyl triflate 12 and iodo-vinyl triflate 13 under standard conditions (TF$_2$O / Pr$_3$NEt / CH$_2$Cl$_2$, Scheme 1). Both 12 and 13 were submitted to a double palladium-catalyzed cross-coupling reaction with two equivalents of HSCH$_2$CH$_2$CO$_2$Et. The iodo derivative 13 gave a complex mixture after the reaction.

Table 1. Synthesis of 1 by a double Pd-catalyzed cross-coupling reaction

<table>
<thead>
<tr>
<th>Entry</th>
<th>cat. (equiv.)</th>
<th>R'SH (equiv.)</th>
<th>Pr$_3$NEt (equiv.)</th>
<th>solvent</th>
<th>1/14$^\text{[b]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(OAc)$_2$ (0.1)</td>
<td>2.2</td>
<td>3</td>
<td>dioxane</td>
<td>no reaction</td>
</tr>
<tr>
<td>2</td>
<td>Pd(dbcat)$_2$ (0.1)</td>
<td>2.2</td>
<td>3</td>
<td>DMF</td>
<td>57/43</td>
</tr>
<tr>
<td>3</td>
<td>Pd(dbca)$_3$ (0.05)</td>
<td>2.2</td>
<td>3</td>
<td>DMF</td>
<td>51/49</td>
</tr>
<tr>
<td>4</td>
<td>Pd(dbca)$_3$ (0.1)</td>
<td>4</td>
<td>5</td>
<td>dioxane</td>
<td>58/42</td>
</tr>
<tr>
<td>5</td>
<td>Pd(dbca)$_3$ (0.05)</td>
<td>4</td>
<td>5</td>
<td>dioxane</td>
<td>54/46</td>
</tr>
<tr>
<td>6</td>
<td>Pd(dbca)$_3$ (0.1)</td>
<td>2.2</td>
<td>3</td>
<td>dioxane</td>
<td>75/25 (66/21)$^\text{[b]}$</td>
</tr>
<tr>
<td>7</td>
<td>Pd(dbca)$_3$ (0.05)</td>
<td>2.2</td>
<td>3</td>
<td>dioxane</td>
<td>88/12 (77/8)$^\text{[b]}$</td>
</tr>
</tbody>
</table>

$^\text{[a]}$The ratios are determined by \(^1\)H NMR spectroscopy. $^\text{[b]}$The yields correspond to isolated products.
However, starting with 12, it was possible to isolate the protected dithiolene ligand 1, along with the mono-substituted product 14 (Table 1). As expected, the vinyl triflate function was more reactive than the vinyl bromide one. In order to optimize the yield of 1, different conditions (solvents, catalysts and the amount of the thiol) were tested. The results are listed in Table 1. The best result was obtained with Pd$_2$(dba)$_3$ (5 %) and Xantphos (10 %) in dioxane in the presence of 2.2 equiv. of HSC$_2$H$_2$CO$_2$Et and 3 equiv. of Pr$_2$NET at 110 °C (entry 7). Under the same conditions, Pd(dba)$_2$ (10 %) gave a slightly lower yield of 1 (entry 6). Pd(OAc)$_2$ did not catalyze this reaction (entry 1). DMF is a less good solvent than 1,4-dioxane (entries 2 and 3). Finally, the isolated compound 14 could be again transformed to 1 in 75 % yield under the same conditions. Both 1 and 14 are fully characterized, especially by $^1$H and $^{13}$C NMR spectroscopy (Figure S1- S4, Supporting Information). Thus, we show for the first time that this cross coupling reaction leading to sulfurated compounds can be extended to functionalized vinyl derivatives.

2. Complexation and reactivity of 1 towards Mo$^{IV}$ ion

1 was treated with $t$BuOK under anaerobic conditions to generate the dithiolene ligand qpd$t^2$ (Figure 1). Due to its instability, this latter was not isolated and was directly reacted with K$_2$Na[MoO$_2$(CN)$_4$]$_2$6H$_2$O$_{12}$ to afford the square planar pyramidal, mononuclear complex (Bu$_4$N)$_2$[Mo$^{IV}$O(qpd$t$)$_2$] (2, Figure 2) after cation exchange with Bu$_4$NBBr.$^{[6]}$

![Figure 2. The Mo-oxo complex (Bu$_4$N)$_2$[Mo$^{IV}$O(qpd$t$)$_2$] (2).](image)

2.1. Reactivity of (Bu$_4$N)$_2$[Mo$^{IV}$O(qpd$t$)$_2$] towards protons

Figure 3 shows the UV-Vis spectrum of 50 $\mu$M (Bu$_4$N)$_2$[Mo$^{IV}$O(qpd$t$)$_2$] in acetonitrile (black curve). Additions of TFA: 1equiv. (purple), 2 equiv. (red), 3 equiv. (green), 4 equiv. (blue), 5 equiv. (light blue), 10 equiv. (magenta), 25 equiv. (yellow), 50 equiv. (dark yellow) and 100 equiv. (navy).

The cyclic voltammogram of 2 in CH$_3$CN displays a reversible redox couple at -0.19 V vs. Ag/AgCl electrode that has been assigned to the Mo$^{IV}$/Mo$^{V}$ couple.$^{[8]}$ Addition of TFA triggers a shift of the potential towards more positive potentials, with a slight loss of current intensity (Figure 4). This shift follows the same trend than that of the absorbance at 564 nm for the same number of equivalents in TFA (Figure 5). Similar results have been recently published by Dicks et al.$^{[13]}$ with simplified asymmetric ene-1,2-dithiolate Co complexes, [[($S^2$-Cr$_2$H$_2$)$_2$Co{SC(H)CR$_2$}] (R= pyridine-3-y1 or pyrazine-2-y1). In this work, they observed that the presence of a 5 : 1 excess of TFA facilitated the reduction of the complexes, i.e. the reduction occurred at more positive potentials. This was attributed to the protonation of a pyrazine-2-y1 ring N atom. Our previous DFT calculations showed that N atom of the central cycle of 2 is likely to be the first protonation site.$^{[8]}$ A second protonation on the same cycle can occur however less favorably because of electrostatic repulsion. These protonation events facilitate reduction of 2, explaining the low overpotential observed during photo- and electro- proton reduction catalyzed by 2.

![Figure 3. UV-Vis spectrum of 50 $\mu$M (Bu$_4$N)$_2$[Mo$^{IV}$O(qpd$t$)$_2$] in acetonitrile (black curve). Additions of TFA: 1equiv. (purple), 2 equiv. (red), 3 equiv. (green), 4 equiv. (blue), 5 equiv. (light blue), 10 equiv. (magenta), 25 equiv. (yellow), 50 equiv. (dark yellow) and 100 equiv. (navy).](image)
2.2. Reactivity of (Bu₄N)₂[MoV₆O(qpdt)]₂ towards O₂

In solution (CH₂CN or CDCl₃), complex 2 is sensitive to O₂. The yellow-green color turned almost instantaneously to orange under exposure to air. The oxidized product was isolated and characterized as the dithiin derivative 15. Single crystals were obtained as orange plates by slow evaporation of an acetonitrile solution containing the crude product. An ORTEP diagram of the molecular structure of 15 shown in Figure 6 reveals a highly conjugated molecule with nearly all the atoms in one plane.

![Figure 6. Crystal structure (ellipsoids drawn at 50% probability) of 15 (A) with nearly all the atoms in one plane (B). Hydrogen atoms are omitted for clarity.](image)

The proposed mechanism for the formation of 15 is depicted in Scheme 3. During the oxidative dimerization reaction, 2 first lost its metal ion to form the bis-disulfide 16, then a rearrangement took place to give the more stable dithiin 15 by elimination of two sulfur atoms of the ligand. This hypothesis was confirmed by positive-ion electrospray mass spectra of 2 in acetonitrile solution upon exposure to air after 1 and 30 minutes, respectively. A peak at m/z = 549 (corresponding to [16 + H⁺]) in the first case (Figure S8), and another one at m/z = 485 (corresponding to [15 + H⁺]) in the second case (Figure S9), were observed. This mechanism is comparable to the previously reported one for the air oxidation of disodium dimercaptomaleodinitrile (Na₂-mnt) giving tetracyano-1,4-dithiin as the product. To our knowledge, it is the first time that the air oxidation product of a MoIV(dithiolene)₂ complex was structurally characterized.

![Scheme 3. Formation of dithiin 15 from [MoV₆O(qpdt)]²⁺ under air oxidation.](image)
2.3. Reactivity of qpdt\(^2\) towards [MoCl\(_4\)(fBuNC)\(_2\)]

The de-protected ligand qpdt\(^2\) was allowed to react with another Mo\(^{4+}\) reagent [MoCl\(_4\)(fBuNC)\(_2\)], in order to generate a new bis-dithiolene bis-isocyanide Mo\(^{IV}\) complex [Mo\(^{IV}\)(qpdt)\(_2\)(fBuNC)\(_2\)] (17, Scheme 4), by a previously reported procedure.\(^{[14]}\) The starting [MoCl\(_4\)(fBuNC)\(_2\)] was generated \textit{in situ} by [MoCl\(_4\)(CH\(_3\)CN)\(_2\)] and an excess of fBuNC. However, no trace of 17 could be detected by electrospray mass spectroscopy. A new tetracyclic imino-thiazole derivative 18 was isolated instead. Single-crystal X-ray analysis of 18\(^{[14]}\) revealed a quite original tetracyclic structure with a C=S bond on the pyran ring (Figure 7).

In a separate experiment, the qpdt\(^2\) ligand was treated with fBuNC in the absence of [MoCl\(_4\)(CH\(_3\)CN)\(_2\)] and 18 was not observed by \(^1\)H NMR spectroscopy. The proposed mechanism is outlined in Scheme 4. We suggest that due to the presence of the neighboring nitrogen atom, a rearrangement took place after the formation of complex [Mo(qpdt)\(_2\)(fBuNC)\(_2\)] 17, leading to the original tetracyclic imino-thiazol 18.

Scheme 4. A proposed mechanism for the formation of 18.

Conclusions

We have developed an unprecedented efficient method to synthesize a bio-inspired dithiolene ligand which is closely related to the biological molybdopterin ligand. The corresponding Mo-oxo complex, which nicely mimics the active site of Mo-enzymes, with Mo being bis-coordinated by this ligand was also obtained.\(^{[8]}\) Investigation of the reactivity of the Mo-dithiolene assembly towards protons, oxygen and isocyanides led to new reactions and original products, which have been spectroscopically and structurally characterized. This provides new insights into Mo-dithiolene chemistry which might have some biological relevance.

Experimental Section

General methods

All starting materials were commercially available and were used without further purification. Solvents were purified by an MBRAUN SPS-800 Solvent Purification System. All reactions were carried out under air atmosphere unless specified. \(^{13}\)C NMR spectra were recorded on a Bruker Avance-III 300 NMR spectrometer (300 MHz for \(^1\)H, 75 MHz for \(^{13}\)C) at room temperature. High-resolution mass spectra (HRMS) were recorded on a LCT Premier XE mass spectrometer using ESI (electrospray ionization) at Institut de Chimie des Substances Naturelles in Gif-sur-Yvette. Mass spectra (MS) were recorded on an Applied Biosystems QSTAR pulsar I mass spectrometer using ESI (electrospray ionization) at Muséum National d’Histoire Naturelle (Paris). Flash chromatography was performed on Grace Reverlis\(^{[8]}\) x2 with corresponding cartridges. UV-Vis spectra were recorded using a Cary 100 UV-Vis spectrophotometer instrument (Agilent). Voltammetric measurements were performed using a SP 300 Bio-Logic potentiostat (Bio-Logic Science Instruments SAS). All measurements were conducted using a three electrode system. A platinum wire, a glassy carbon (1 mm diameter) and a saturated Ag/AgCl/KCl saturated electrode were used as counter and reference electrodes, respectively. Cyclic voltammograms were recorded in anhydrous acetonitrile (Sigma) containing 0.1 M tetrabutylammonium perchlorate (TBAP, Sigma) in anaerobic conditions at room temperature. Synthesis of 3, 7 and 12 were reported earlier.\(^{[8]}\)

4-(3-chloroquinoxalin-2-yl)-2-methylbut-3-yn-2-ol (5)

Under an Ar atmosphere, to a solution of 2,3-dichloroquinoxaline (10 g, 50.2 mmol) in dry THF (45 mL) were added Cul (619 mg, 3.26 mmol) and PdCl\(_2\)(PPPh\(_3\))\(_2\) (1.056 g, 1.51 mmol). \(\text{PdCl}_2\) (16.6 mL, 95.38 mmol) was slowly added via a syringe to give an orange suspension. 2-methylbut-3-yn-2-ol (4.217 g, 50.2 mmol) was then slowly added to the mixture via a cannula needle. The suspension was stirred at room temperature overnight and led to a dark orange suspension. The reaction mixture was concentrated in \textit{vacuo} and extracted with CH\(_2\)Cl\(_2\) three times. The combined organic layers were dried over magnesium sulfate and concentrated in \textit{vacuo}. Purification of
the crude product by flash chromatography over silica gel using EiOAc : cyclohexane (1 : 4) as an eluent gave a brown oil (10.452 g, 84 %). 1H NMR (CDCl3) δ 8.11 (m, 1H, Ar), 8.02 (m, 1H, Ar), 7.86 – 7.74 (m, 2H, Ar), 2.39 (s, 1H, D2O exchangeable, OH), 1.74 (s, 6H, CH3). This spectrum was identical to the previously reported one.3

3-Methoxy-2,2-dimethyl-2H-1-oxa-9,10-diaza-anthracene (6). Under an Ar atmosphere, sodium hydride (60 % in mineral oil, 8.48 g, 212 mmol) was added in small portions to methanol (66 mL) at 0° C. The white suspension was allowed to stir for 10-15 minutes at room temperature until no more gas evolution could be observed. A solution of 5 (10.452 g 42.4 mmol) in 17 mL of methanol was slowly added via a cannula needle. The green/dark suspension was stirred at 80 °C for 1.5 h. MeOH was evaporated under reduced pressure. The usual work-up with EiOAc gave a crude product, which was purified by flash chromatography over silica gel (eluting with EiOAc : cyclohexane, 15 : 85). 5.951 g (58 %) was obtained. 1H NMR (CDCl3) δ 7.86 (m, 1H, Ar), 7.78 (m, 1H, Ar), 7.52 (m, 2H, Ar), 5.95 (s, 1H, CH3). 13C NMR (CDCl3) δ 157.38 (C), 151.21 (C), 141.31 (C), 140.52 (C), 137.21 (C), 131.61 (CH), 129.18 (CH), 128.32 (CH), 127.23 (CH), 118.50 (q, JF = 321.4 Hz, CF3). 94.73 (C), 82.18 (C), 26.05 (2 CH3). HRMS: m/z calcd. for C18H17F3N2O2S [M + H]+: 486.9436; found: 486.9475.

3,4-bis(Ethoxy carbonyl-ethyl)sulfanyl)-2,2-dimethyl-2H-1-oxa-9,10-diaza-anthracen-3-yl ester (14). Under an Ar atmosphere, in a 250 mL Schlenk flask, a mixture of 12 (3 g, 6.83 mmol), Xantphos (395 mg, 0.683 mmol) and Pd(dbach)2 (393 mg, 0.683 mmol) in dry 1,4-dioxane (60 mL) was degassed under Ar for 30 min. Pr2Net (3.6 mL, 20.5 mmol) and HSC6H3Cl2CHOEt (1.9 mL, 15 mmol) were then added. The brownish mixture was gently degassed under Ar for 10 min. and kept at 110° C for 3.5 h. The reaction mixture was evaporated to dryness. The usual work-up with CH2Cl2 gave a crude product, which was purified by flash chromatography over silica gel (eluting with AcOEt : cyclohexane 5 : 95). 1 (a brown oil, 208 g, 64 %) and 14 (a brown oil, 535 mg, 19 %) were obtained.

1H NMR (CDCl3): δ 0.06 (dd, J = 1.5, 8.0 Hz, 1H, Ar), 7.83 (dd, J = 1.5, 8.0 Hz, 1H, Ar), 7.66 (m, 1H, Ar), 7.59 (m, 1H, Ar), 4.17 (q, J = 7.0 Hz, 2H, CH2), 4.10 (q, J = 7.0 Hz, 2H, CH2), 3.33 (t, J = 7.0 Hz, 2H, CH2), 3.31 (t, J = 7.0 Hz, 2H, CH2), 2.67 (t, J = 14.1 Hz, 2H, CH2), 1.47 (s, 6H, CH3), 1.27 (t, J = 7.0 Hz, 3H, CH3), 1.21 (t, J = 7.0 Hz, 3H, CH3), 0.19 mmol) in dry 1,4-dioxane (1 mL) was degassed under Ar for 30 min. Pr2Net (57 μL, 0.326 mmol) and thiacetonic acid (14 μL, 0.196 mmol) were then added. The brownish mixture was gently degassed under Ar for 10 min and kept at 80° C for 3 h. The reaction mixture was evaporated to dryness. The usual work-up with CH2Cl2 gave a crude product, which was purified by flash chromatography over silica gel (eluting with THF : cyclohexane, 5 : 95) to give 10 as a yellow powder (37 %, 77 g).

13C NMR (CDCl3) δ 12.50 (s, 2H, D2O exchangeable, CH3OH); 7.74-7.60 (m, 4H, Ar), 7.52-7.44 (m, 2H, Ar), 7.43-7.33 (m, 2H, Ar), 1.78 (s, 6H, 2 CH3). 13C NMR (CDCl3) δ 192.42 (C), 152.60 (C), 141.11 (C), 134.48 (C), 128.46 (C), 128.42 (C), 127.24 (C), 126.07 (CH), 116.63 (CH), 94.93 (C), 86.88 (C), 27.15 (4 CH3). HRMS: m/z calcd. for C30H24N2O2S [M + H]+: 487.1440; found: 487.1423.

Trifluoro-methanesulfonic acid 4-iodo-2,2-dimethyl-2H-1-oxa-9,10-diaza-anthracen-3-yl ester (13). Under an Ar atmosphere, to a solution of 3 (155 mg, 0.438 mmol) and Pr2NEt (115 μL, 0.657 mmol) in dry CH2Cl2 (3 mL) was added at 0 °C dropwise triflic anhydride (161 mg, 0.569 mmol). After 20 minutes at room temperature, water (1 mL) was added and the usual work-up with CH2Cl2 gave a crude product, which was purified by flash chromatography over silica gel (eluting with CH2Cl2) to yield a white powder (135 mg, 64 %). 1H NMR (CDCl3) δ 8.14 (dd, J = 1.0, 8.0 Hz, 1H, Ar), 7.90 (dd, J = 1.0, 8.0 Hz, 1H, Ar), 7.71 (m, 2H, Ar), 1.79 (s, 6H, 2 CH3). 19F NMR (CDCl3) δ 157.38 (C), 151.21 (C), 141.31 (C), 140.52 (C), 137.21 (C), 131.61 (CH), 129.18 (CH), 128.32 (CH), 127.23 (CH), 118.50 (q, JF = 321.4 Hz, CF3). 94.73 (C), 82.18 (C), 26.05 (2 CH3). HRMS: m/z calcd. for C18H17F3N2O2S [M + H]+: 486.9436; found: 486.9475.
was added NaH. 1H NMR (CDCl3): δ 8.07 (dd, J = 1.5, 8.0 Hz, 1H, Ar), 7.84 (dd, J = 1.5, 8.0 Hz, 1H, Ar), 7.64 (m, 2H, Ar), 1.89 (s, 6H, 2 CH3). 13C NMR (CDCl3): δ 152.71 (C), 143.87 (C), 140.92 (C), 139.56 (C), 135.82 (C), 130.36 (CH), 128.87 (CH), 127.69 (CH), 127.30 (CH), 122.67 (C), 83.54 (m/z calcd. for C36H31N4O2S2[M + H]+: 358.1048; found: 358.1061.

Imino-thiazol compound 18. The experience was carried out thoroughly under an Ar atmosphere by using Schlenk flasks and all solutions were degassed prior to use. To a suspension of [MoCl4(CH3CN)2]3−(50 mg, 0.155 mmol) in anhydrous THF (10 mL) was added BuNC (141 μL, 1.25 mmol). After 15 min., [MoCl4(BuNC)4] was formed in situ as a pink solution. Meanwhile and in a separate Schlenk flask, to a solution of 1 (148 mg, 0.31 mmol) in anhydrous THF (3 mL) was added NaH (50 mg, 60 % in mineral oil, 1.24 mmol) at 0 °C. After 15 min. at room temperature, the dark red solution was slowly transferred to the [MoCl4(BuNC)4] solution via a cannula needle. The color turned to dark brown immediately. The reaction was allowed to stir at room temperature for 1 night. Evaporation of THF in vacuo gave a crude product, which was purified by flash chromatography over silica gel (eluting with CH2Cl2) to furnish a red solid (71 mg, 64 %). Single crystals were grown by slow evaporation of CH2Cl2 containing the product. UV–vis (CH2CN) λmax (nm) 524 (11800), 494 (8720), 452 (3620) sh, 423 (1820) sh, 300 (3620). 1H NMR (CDCl3): δ 9.78 – 9.47 (m, 1H, Ar), 7.70 – 7.59 (m, 1H, Ar), 7.51 – 7.34 (m, 2H, Ar), 1.94 (s, 6H, 2 CH3), 1.49 (s, 9H, 3 CH3). 13C NMR (CDCl3): δ 208.89 (C=S), 152.93 (C), 145.81 (C), 137.22 (C), 128.39 (C), 127.87 (CH), 127.51 (CH), 127.16 (CH), 123.03 (C), 121.23 (C), 118.28 (CH), 96.42 (C), 56.18 (C), 31.07 (2 CH3), 27.49 (3 CH3). HRMS: m/z calcd. for C16H26N5O2S2 [M + H]+: 358.1048; found: 358.1061.

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Keywords: dithioleone ligands • molybdenum • C–S cross-coupling • cyclic voltammetry • palladium

[14] CCDC 1430930 and 1430931 contain the supplementary crystallographic data for 15 and 18. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.