METAL COMPLEXES OF AN AMINE BISPHENOL WITH A THIOPHENE SIDE-ARM

Eero SALMINEN[a1], Reijo SILLANPÄÄ[b] and Ari LEHTONEN[a2,*]

[a] *Laboratory of Materials Chemistry and Chemical Analysis, Department of Chemistry, University of Turku, FI-20014 Turku, Finland; e-mail: [1] essalm@utu.fi, [2] arileh@utu.fi*

[b] *Laboratory of Inorganic Chemistry, Department of Chemistry, University of Jyväskylä, FI-40351 Jyväskylä, Finland; e-mail: resillan@jyu.fi*

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Dedicated to Professor Bohumil Štíbr on the occasion of his 70th birthday in recognition his outstanding contributions to the field of organometallic chemistry.

Dioxomolybdenum(VI) and oxotungsten(VI) complexes with a new amine bisphenol ligand (H_2L) are reported. The ligand which carries a neutral nitrogen atom, two phenolic oxygen atoms and a thiophene side-arm was synthesized by a simple one-pot Mannich reaction. Further reaction with $[MoO_2(acac)_2]$ yielded a monomeric molybdenum complex $[MoO_2(L)(MeOH)]$ (**2a**) or a dimeric complex $[Mo_2O_2(\mu\text{-}O)_2(L)_2]$ (**2b**), depending on the reaction conditions. The reaction with a tungsten trisglycolate $[W(eg)_3]$ led to the formation of a monomeric compound [WO(eg)(L)] (**3**). In these complexes, the potentially tetradentate amine bisphenolate dianion coordinates as a tridentate O,N,O donor while the sulfur side-arm donor remains intact. The solid-state structure of **2a** was investigated by X-ray crystallography.

Keywords: Tungsten; Molybdenum; Phenolate ligands.

In organometallic chemistry, several bulky anionic ligands with hard oxygen donor atoms have been used to control the structure and reactivity of metal complexes and various phenolate ligands, especially, have shown great promise towards this goal[1]. For instance, amine bisphenol molecules form a group of readily available and versatile chelating ligands[2]. Especially, tripodal ligands with an attached side-arm donor are complexed with several main-group and transition metals to form active catalysts and initiators for various biomimetic processes as well as some industrially valuable reactions. For example, in studies on bioinorganic chemistry, Cu(II) complexes supported by a tripodal N_2O_2 donor set are used as functional analogues for galactose oxidase[3]. Similarly, several Fe(III) complexes containing

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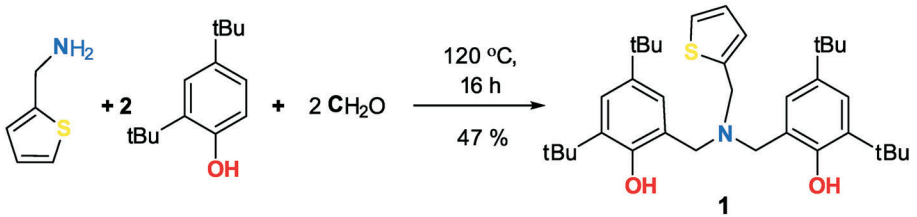
amine bisphenol ligands with a pyridyl side-arm were reported as synthetic models for catechol dioxygenases[4]. A number of transition metal complexes with this type of ligands have been studied due to their relevance in industrial applications. Such examples are zirconium catalysts for olefin polymerization[5] and titanium catalysts for the ring-opening polymerization of lactones[6]. Dioxomolybdenum(VI) and dioxotungsten(VI) complexes with tripodal or linear amine bisphenols resemble the active centres of several metal based enzymes, thus they can be used as model compounds in biological oxotransfer reactions[7,8]. The reactivity of such compounds can be also employed in industrially important reactions, e.g. in epoxidation of olefins[9]. Amine bisphenols with a coordinating side-arm group combine typically hard nitrogen and oxygen donors to react as dianionic, tetradentate chelators[10]. In this paper we report a synthesis of a new potentially tetradentate amine bisphenol with a thiophene side-arm. The final aim was to combine hard oxygen and nitrogen donors with a soft sulfur donor to have a biomimetic O_2NS donor set around a metal centre. It was found that the new amine bisphenol molecule reacts with molybdenum(VI) and tungsten(VI) precursors as a tridentate O,N,O donor while the sulfur side-arm donor remains uncoordinated.

RESULTS AND DISCUSSION

Syntheses

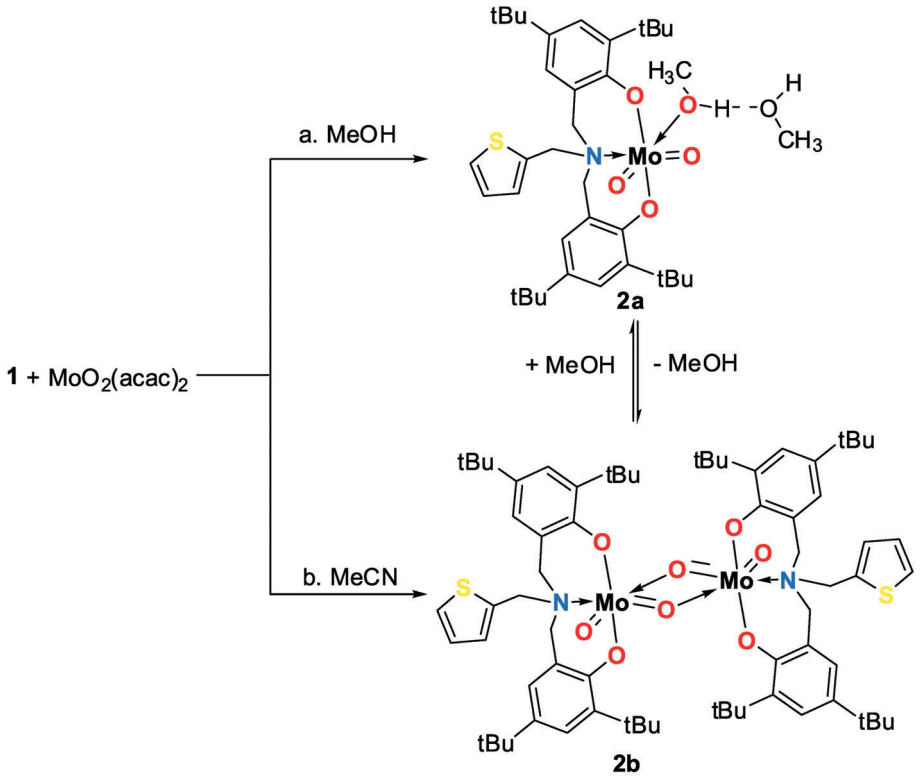
The amine bisphenol **1** was prepared straightforwardly by a solvent-free Mannich reaction[11]. A mixture of 2,4-di-*tert*-butylphenol, 2-(aminomethyl)-thiophene and paraformaldehyde was kept at 120 °C for 16 h and the resulting solid material was recrystallized from acetonitrile (Scheme 1).



SCHEME 1

The product formed in the reaction between $[MoO_2(acac)_2]$ and a ligand **1** was found to depend on the reaction medium (Scheme 2). When a methanol solution of $[MoO_2(acac)_2]$ was treated with one equivalent of **1**, the re-

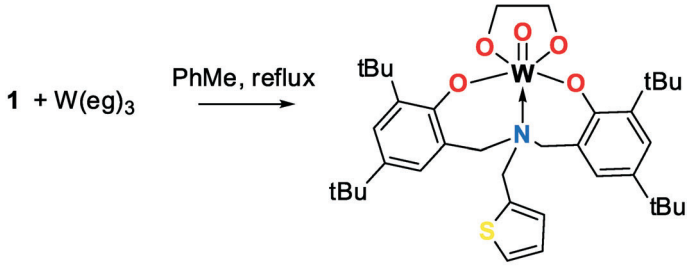
action initiated and the reaction mixture subsequently turned yellow in colour (Scheme 2a). The solution was kept at 4 °C for 24 h to obtain yellow prismatic crystals, which were characterized by XRD as $[MoO_2(L)(MeOH)]\cdot MeOH$ (**2a**). The corresponding solvate complex was formed also in dimethylsulfoxide (DMSO) solution. When the identical reaction was carried out in the acetonitrile solution, the reaction mixture turned orange-red and orange microcrystals started to precipitate (Scheme 2b). Elemental analyses and spectroscopic measurements showed that the crystals were formed of dimeric complexes $[Mo_2O_2(\mu\text{-}O)_2(L)_2]$ (**2b**). The slightly air-sensitive **2a** is soluble in DMSO, DMF and hot MeOH, but it reacts in an acetonitrile suspension to form a dimeric complex **2b** as a red powder. Similar deformation occurs also in open air and particularly in vacuum due to the loss of methanol solvate molecules. Air-stable crystals of **2b** dissolve in DMSO to yield yellow solutions, but they are practically insoluble in other common solvents at room temperature. Compound **2b** dissolves also in methanol upon



Scheme 2

heating while recrystallization from hot methanol produces the methanol adduct **2a**. In conclusion, it is demonstrated that the formation of complexes **2a** and **2b** can be easily adjusted. Particularly, the monomeric complex is transformed to the dimeric counterpart as a consequence of the leaving of methanol in the solid state, whereas the dimeric form can be turned to the monomeric one by recrystallization from MeOH. As MeOH and MeCN have practically the same steric properties, the coordinating capability of MeOH and the formation of hydrogen bonds seem to have significant roles in the formation of the monomeric adduct. This solvent-dependent reactivity resembles the reactions of $[MoO_2(acac)_2]$ with related tridentate dianionic ligands[12,13].

The tungsten complex **3** was prepared by applying the reaction conditions reported earlier for the preparation of related amine bisphenol complexes[14]. The stirred suspension of a tungsten precursor $[W(eg)_3]$ (eg = 1,2-ethanediolate dianion) in toluene was treated with a stoichiometric amount of the ligand **1** at reflux temperature while the reaction was promoted by fractionating out the liberated 1,2-ethanediol as a toluene azeotrope (Scheme 3). The ^{1}H NMR spectrum of the unpurified yellow reaction mixture shows resonances for **3** along with some uncharacterized minor components. The oxotungsten(VI) complex **3** was isolated by column chromatography and crystallized from hot toluene as bright yellow crystals. As expected on the grounds of our earlier studies on amine bisphenolate complexes of tungsten(VI), the coordination of ligand **1** was associated with the formation of an oxo group[14]. Although the formation of terminal oxo group was predictable due to our earlier investigations, the source of the oxo moiety remains unclear. In principle, high-valent metal alkoxides can decompose by an elimination process, which yields ether and the corresponding oxometal compounds[15]. However, water is the most likely source of oxide, as it is practically impossible to exclude the diminutive amount of water necessary to carry out the hydrolysis reaction.



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SCHEME 3

Solution and Solid-State Structures

In the solid state, complex **2a** is formed of mononuclear units, in which the amine bisphenolate is coordinated to the dioxomolybdenum(VI) ion as a tridentate ligand. In the solid state, complex **2a** is formed of mononuclear units, in which the amine bisphenolate is coordinated to the dioxomolybdenum(VI) ion as a tridentate ligand. The coordination sphere around the central metal presents distorted octahedral geometry with the terminal oxo ligands *cis* to each other. Two anionic phenolate oxygens and two neutral donor atoms of the ligands are *trans* and *cis*, respectively, as expected for octahedral dioxo complexes. The Mo1–O5 and Mo1–N8 bonds are relatively long (2.338(2) and 2.499(2) Å, respectively), which can be explained by the strong *trans*-effect of the oxo ligands[7]. A thiophene sidearm donor does not coordinate to the metal centre. Instead, a molecule of solvent methanol is located *trans* to the oxo group to complete the coordination sphere (Fig. 1). Another molecule of methanol is attached to the co-

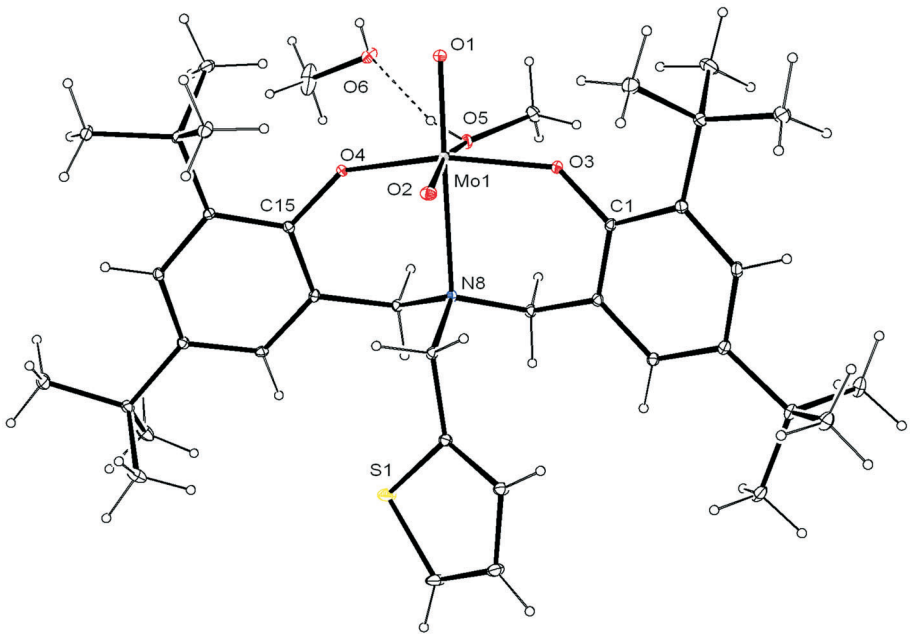

FIG. 1
Molecular structure of $[MoO_2(L)(MeOH)]\cdot MeOH$ (**2a**). Thermal ellipsoids have been drawn at 30% probability level. Selected bond lengths (in Å) and angles (in °): Mo1–O1 1.7114(19), Mo1–O2 1.6945(19), Mo1–O3 1.9241(18), Mo1–O4 1.9153(18), Mo1–O5 2.338(2), Mo1–N8 2.499(2); O1–Mo1–O2 105.06(10), O1–Mo1–N8 168.34(9), O2–Mo1–O5 166.14(8)

ordinated methanol through hydrogen bonding (coordinated MeOH as an acceptor) with the O···O distance of 2.597 Å. The uncoordinated MeOH molecule forms a hydrogen bond with terminal oxygen atom O1 of the adjacent unit, the O···O distance being 2.731 Å. The O=Mo=O angles and the Mo=O bonds are typical for *cis*-dioxomolybdenum(VI) phenolates[7,9,12,16–18]. Also the Mo–O(phenolate) bond lengths (1.9241(18) and 1.9153(18) Å) and Mo–O–C angles (134.80(16) and 140.18(17)°) are similar to those reported for other dioxomolybdenum(VI) phenolate complexes. According to our earlier investigations on the related complexes of tridentate amine bisphenols[12], we may suggest that complex **2b** consists of dinuclear, doubly bridged units of $Mo_2O_2(\mu\text{-}O)_2(L)_2$. The IR spectrum of **2a** presents strong bands at 900 and 922 cm^{-1}, which are distinctive absorption maxims for MoO_2^{2+} moiety[19]. Bands at ~3440 and 3640 cm^{-1} are due to the presence of coordinated and hydrogen bonded methanol molecules. Complex **2b** has generally similar IR spectrum although it presents a strong IR absorption at 834 cm^{-1}, which is typical for a non-symmetrically bridged Mo–O–Mo core[20]. Furthermore, complexes **2b** show only a single stretch at 941 cm^{-1} instead of a characteristic doublet for *cis*-MoO_2 moieties in complexes **2a**. ^1H NMR spectrum of **2a** in DMSO shows typical resonances for C_s-symmetric amine bisphenolate complexes together with resonances for free methanol, which indicates that DMSO can replace MeOH molecules from the first coordination sphere around Mo(VI) ion. The DMSO-d_6 solutions of compounds **2a** and **2b** show identical ^1H and ^{13}C NMR resonances for the chelate ligand, so it seems evident that the supposed dimeric structure of **2b** breaks down upon dissolution in DMSO. In both cases, the ^1H NMR spectrum shows doublets for the methylene protons bridging the phenolates and the central amine nitrogen. This confirms that these protons are diastereotopic, i.e. on each methylene group one proton faces towards the thiophene and the other faces away from it. A singlet for the methylene protons adjacent to the thiophene group indicates that these protons are equivalent, so the thiophene sulfur seems not to coordinate to the metal centre to form a chelate ring.

Spectroscopic analyses of yellow product **3** indicate that the simple alkoxide displacement reaction of trisglycolate [$W(eg)_3$] is associated with some other modification in the ligand environment, i.e. the formation of an oxo group. ^1H NMR spectrum showed anticipated resonances for coordinated amine bisphenolate ligand. The CH_2 protons were seen as broad overlapping signals at 3.7–4.0 ppm. Similar resonances are found earlier for structurally well-characterized amine bisphenolate complexes of oxotungsten(VI) with a *cis*-orientation of phenolate moieties. In the aliphatic

region of the spectra two distinct multiplets for the ethanediolate groups are observed implying that there are two different environments for these methylene protons. The different signals for the axial and equatorial hydrogen atoms are indications of a rigid glycolate chelate ring, which prevents the fast transformations of the ligand configuration. IR spectrum shows a strong absorption band at 953 cm^{-1}, which is typical for a W=O moiety.

CONCLUSIONS

A new amine bisphenolate, which carries a neutral nitrogen atom, two phenolic oxygen atoms and a thiophene side-arm, was synthesized by a simple one-pot Mannich reaction. The reaction of a new ligand with $[MoO_2(acac)_2]$ in a methanol solution yields a monomeric molybdenum complex $[MoO_2(L)(MeOH)]$, whereas a dimeric complex $[Mo_2O_2(\mu\text{-}O)_2(L)_2]$ is formed in acetonitrile. The reaction with a tungsten trisglycolate $[W(eg)_3]$ in toluene leads to the formation of a monomeric compound [WO(eg)(L)]. In all cases, the amine bisphenolate dianion coordinates as a tridentate O,N,O donor while the sulfur side-arm donor remains intact.

EXPERIMENTAL

Starting complexes $[MoO_2(acac)_2]$ and $[W(eg)_3]$ were prepared according to the literature procedures[21,22]. Other chemicals and solvents were obtained from commercial sources and were used as purchased. IR spectra (ν, cm^{-1}) were measured in KBr using a diffusion reflectance attachment. The NMR spectra (δ, ppm; *J*, Hz) were recorded at 25 °C with a Bruker Avance 400 spectrometer (^1H at 399.75 MHz, ^{13}C at 100.52 MHz) equipped with a broadband observe probe (BBO-5mm-Zgrad) and referenced internally to TMS.

6,6′-(Thiophen-2-ylmethylazanediyl)bis(methylene)bis(2,4-di-*tert*-butylphenol) (**1**)

2,4-Di-*tert*-butylphenol (8.25 g, 40.0 mmol), 2-(aminomethyl)thiophene (2.26 g, 20 mmol) and paraformaldehyde (1.32 g, 44 mmol) were mixed in an open vessel and the reaction mixture was kept at 120 °C for 16 h. The sticky mixture was cooled to the room temperature, mixed with 15 ml of acetonitrile and then kept overnight at –18 °C. Colorless crystalline material was separated by filtration and washed with cold acetonitrile to obtain 5.11 g (47%) of amine bisphenol **1**, m.p. 126 °C. ^1H NMR ($CDCl_3$): 1.303 s, 18 H (*t*-Bu); 1.439 s, 18 H (*t*-Bu); 3.718 s, 4 H (CH_2); 3.875 s, 2 H (CH_2); 6.97–7.44, five partially overlapping signals, 5 H (ArH + thiophene); 10.5 s (br.), 2 H (ArO**H**). ^{13}C NMR ($CDCl_3$): 29.67 (C**Me**$_3$); 31.64 (C**Me**$_3$); 34.19 (**C**Me$_3$); 34.91 (**C**Me$_3$); 51.73 (CH_2); 56.37 (CH_2); 121.16, 123.67, 125.23, 126.06, 127.15, 127.98, 136.04, 139.37, 141.52, 152.28. For $C_{35}H_{51}NO_2S$ (549.87) calculated: 76.45% C, 9.35% H, 2.55% N; found: 76.73% C, 9.02% H, 2.56% N.

$[MoO_2(L)(MeOH)]\cdot MeOH$ (**2a**)

$[MoO_2(acac)_2]$ (163 mg, 0.50 mmol) and a ligand **1** (275 mg, 0.50 mmol) were dissolved in 10 ml of methanol by a gentle heating. The yellow reaction mixture was stored at –18 °C for 2 days. Yellow crystals formed were isolated and washed with cold methanol to obtain 243 mg (72%) of molybdenum complex **2a**. The NMR sample was prepared by adding the complex in excess, and then filtering away the undissolved part, thus the amounts of MeOH in a sample was not stoichiometric. ^{1}H NMR (DMSO-d_6): 1.290 s, 18 H (*t*-Bu); 1.409 s, 18 H (*t*-Bu); 3.17 d, *J* = 5.2, 18 H (**Me**OH); 3.368 d, *J* = 13.2, 2 H ($ArCH_2$); 4.057 s, 2 H (thiophene-CH_2); 4.09 q, *J* = 5.2, 6 H (MeO**H**); 4.240 d, *J* = 13.2, 2 H ($ArCH_2$); 6.557 d, *J* = 2.4, 1 H (thiophene); 7.012 s, 1 H (ArH); 7.025, overlapping s + t, 3 H (ArH + thiophene); 7.250 s, 2 H (ArH); 7.665 d, *J* = 5.2, 1 H (thiophene). ^{13}C NMR (DMSO-d_6): 30.02 (C**Me**$_3$); 31.36 (C**Me**$_3$); 33.88 (**C**Me$_3$); 34.60 (**C**Me$_3$); 48.50 (CH_2); 55.99 (CH_2); 122.81 (arom.); 122.89 (arom.); 125.89 (thiophene); 126.16 (arom.); 127.88 (thiophene); 131.69 (thiophene); 133.13 (thiophene); 135.91 (arom.); 140.79 (arom.); 159.34 (arom.). IR: 470 w, 570 m, 712 m, 760 s, 801 m, 815 m, 844 vs, 855 m, 883 s, 900 vs, 912 vs, 922 vs, 958 m, 1006 vs, 1012 m, 1080 w, 1124 m, 1168 s, 1208 m, 1236 s, 1257 vs, 1311 m, 1342 m, 1360 m, 1474 s, 2867 m, 2909 s, 2959 vs, 3406 s, 3638 s. For $C_{37}H_{57}MoNO_6S$ (739.86) calculated: 60.07% C, 7.77% H, 1.89% N; found: 59.74% C, 7.36% H, 1.94% N. Elemental analyses gave erroneous results for **2a** due to the partial loss of solvent molecules upon work-up.

$[Mo_2O_2(\mu\text{-}O)_2(L)_2]$ (**2b**)

$[MoO_2(acac)_2]$ (98 mg, 0.30 mmol) and ligand **1** (165 mg, 0.30 mmol) were mixed with 10 ml of acetonitrile. The orange-red reaction mixture was kept at room temperature overnight. The solid product was filtered and washed with acetonitrile to obtain 190 mg (94%) of **2b** as orange-red microcrystals. ^{1}H NMR (DMSO-d_6): 1.290 s, 18 H (*t*-Bu); 1.411 s, 18 H (*t*-Bu); 3.370 d, *J* = 13.2, 2 H ($ArCH_2$); 4.054 s, 2 H (thiophene-CH_2); 4.242 d, *J* = 13.2, 2 H ($ArCH_2$); 6.556 d, *J* = 2.4, 1 H (thiophene); 7.009 s, 1 H (ArH); 7.022, overlapping s + t, 3 H (ArH + thiophene); 7.250 s, 2 H (ArH); 7.666 d, *J* = 5.2, 1 H (thiophene). ^{13}C NMR (DMSO-d_6): 30.00 (C**Me**$_3$); 31.38 (C**Me**$_3$); 33.87 (**C**Me$_3$); 34.59 (**C**Me$_3$); 48.52 (CH_2); 55.99 (CH_2); 122.82 (arom.); 122.92 (arom.); 125.90 (thiophene); 126.20 (arom.); 127.88 (thiophene); 131.68 (thiophene); 133.12 (thiophene); 135.92 (arom.); 140.81 (arom.); 159.32 (arom.). IR: 475 w, 572 m, 700 m, 712 m, 760 s, 807 s, 815 m, 834 vs, 844 vs, 850 vs, 867 s, 882 m, 911 m, 925 m, 941 s, 970 m, 1085 w, 1012 m, 1065 m, 1125 m, 1168 s, 1202 m, 1235 s, 1256 vs, 1309 m, 1342 m, 1359 m, 1390 m, 1474 s, 2865 m, 2900 s, 2952 vs. For $C_{70}H_{98}Mo_2N_2O_8S_2$ (1351.55) calculated: 62.21% C, 7.31% H, 2.07% N; found: 62.11% C, 7.45% H, 2.06% N.

[WO(eg)(L)] (**3**)

$[W(eg)_3]$ (182 mg, 0.50 mmol) and ligand **1** (275 mg, 0.50 mmol) were mixed with 30 ml of toluene. The reaction mixture was stirred under reflux for 2 h. The most of solvent and other volatiles were then removed by distillation and the yellow product was isolated by silica column chromatography using toluene as an eluent. The solid material was crystallized from 5 ml of hot acetonitrile to obtain 254 mg (63%) of **3** as bright yellow crystals. ^{1}H NMR ($CDCl_3$): 1.313 s, 18 H (*t*-Bu); 1.527 s, 18 H (*t*-Bu); 3.7–4.0, several peaks, 4 H ($ArCH_2$); 4.134 s, 2 H (thiophene-CH_2); 5.082 m, 2 H (OCH_2); 5.294 m, 2 H (OCH_2); 6.984 overlap-

ping s + t, 3 H (ArH + thiophene); 7.127 m, 1 H (thiophene); 7.025, overlapping s + t, 3 H (ArH + thiophene); 7.414 d, J = 2.4, 1 H (ArH); 7.465 d, J = 5.2, 1 H (thiophene). ^{13}C NMR ($CDCl_3$): 30.10 (C**Me**$_3$); 31.62 (C**Me**$_3$); 34.54 (**C**Me$_3$); 35.13 (**C**Me$_3$); 51.38 (thiophene-CH_2); 55.99 (ArCH_2); 80.11 (OCH_2); 123.66 (arom.); 125.68 (thiophene); 126.78 (arom.); 127.34 (thiophene); 132.04 (thiophene); 133.02 (thiophene); 135.91 (arom.); 140.23 (arom.); 145.55 (arom.); 154.02 (arom.). IR: 513 m, 562 m, 604 m, 621 s, 715 s, 739 w, 828 m, 869 vs (br); 896 w, 919 s, 953 vs, 968 m, 999 w, 1029 w, 1080 m, 1063 vs, 1170 s, 1021 s, 1129 m, 1238 vs, 1290 m, 1339 m, 1360 s, 1390 m, 1464 s, 1476 s, 2865 m, 2900 s, 2952 vs. For $C_{37}H_{53}NO_5SW$ (807.73) calculated: 55.02% C, 6.61% H, 1.73% N; found: 54.88% C, 6.85% H, 1.72% N.

X-ray Crystallography

The crystallographic data were collected at 173 K on an Enraf Nonius Kappa CCD area detector diffractometer using graphite monochromatized MoKα radiation (λ = 0.71073 Å). Data collection was performed using φ and ω scans and the data were processed using DENZO-SMN v0.93.0 [23]. SADABS [24] absorption correction was applied to the data of all compounds. The structures were solved by direct methods using the SHELXS97 program and full-matrix least-squares refinements on F^2 were performed using the SHELXL97 program[25]. Structure figures were drawn using Ortep-3 for Windows[26]. Summary of crystallographic data for **2a:** Yellow crystals, formula $C_{37}H_{57}MoNO_6S$, crystal system monoclinic, space group $P2_1/n$, a = 11.8839(3) Å, b = 19.6243(4) Å, c = 16.5166(5) Å, β = 101.9920(10)°, V = 3767.83(17) Å^3, Z = 4, $R1$ = 0.0616, $wR2$ = 0.0883, GOF = 1.026.

CCDC 777096 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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