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Research paper

Alkoxylation of the imine carbon atom of a Schiff-base ligand upon coordination to arene ruthenium

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ABSTRACT

The Schiff-base 5-methyl-4-{(pyridin-2-ylmethylene)amino}-4H-1,2,4-triazole-3-thiol (L-H) reacts in alcoholic solution (methanol, ethanol, isopropanol) at room temperature with the dinuclear precursor $[(\eta^6\text{-MeC}_6\text{H}_4\text{Pr}^i)\text{RuCl}_2]_2$ to give a series of neutral complexes of the general formula $(\eta^6\text{-MeC}_6\text{H}_4\text{Pr}^i)\text{Ru(L-OR)}$ (R = Me, **1**; R = Et, **2**; R = Pr^i, **3**). In these complexes, the Schiff-base ligand coordinates to the arene ruthenium unit in a *S,N,N*-tridentate fashion and concomitantly to the coordination process a nucleophilic addition of the alcohol occurs on the imine carbon of L, thus forming the corresponding L-OR ligand. The molecular structure of **3**, solved by single-crystal X-ray analysis, shows a piano-stool arrangement with the *p*-cymene, the $S_{thiolato}$, the N_{imine} and $N_{pyridyl}$ surrounding the chiral-at-metal ruthenium center and an OPr^i group attached to the imine carbon. The insertion of an alkoxy group on the carbon atom reduces the imine function and also introduces chirality on the ligand, thus generating a second chiral center and potentially diastereoisomeric complexes. However, steric hindrance on the ligand forces the formation of only one pair of enantiomers.

1. Introduction

For decades, piano-stool complexes including a chelating ligand have shown particular interest in organometallic chemistry. The structural diversity characterizing these organometallic species allows the development of a wide variety of complexes, different by the nature of the aromatic ligand (benzene, toluene, *p*-cymene, bisphenyl, ethyl benzoate, cyclopentadienyl, pentamethylcyclopentadienyl), the metal ion (Ru, Os, Rh, Ir), as well as by the type of the chelating ligand: polypyridines [1], salicylideneanilines [2], thiosemicarbazones [3], pyrone derivatives [4], phenanthroimidazoles [5]. Among piano-stool complexes with chelating ligands, those incorporating Schiff-bases are of particular importance, because of the range of their physicochemical properties and the extent of their fields of application [6]. Moreover, these chelating ligands are often synthesized under mild reaction conditions with high yields, by the direct condensation of aldehydes with any kind of aliphatic or aromatic primary amines [7], thus providing ligands with customized properties.

Schiff-bases offer multiple denticities and various type of coordination sites (N, O, S), thus coordinating metal ions with high stability constants [8]. In addition, the presence of mixed donor atoms in the Schiff-base gives rise to different or even opposite electronic effects on the central metal ion: Hard donors (N, O) stabilize ions in high oxidation states, while lower oxidation states can be stabilized by soft donors (S, C=N). However, it should be noted that, despite their low basicity and thus their high stability as organic ligands, some aromatic Schiff-bases are likely to undergo, upon coordination with metal ions, a reaction of hydrolysis, transforming them, partially or totally, into their starting reagents [9]. Moreover, the catalytic effect of H^+ and OH^-, as well as the role of the metal ion on the rate of hydrolysis of certain aromatic Schiff-bases, has been previously studied [10].

In addition, several studies concerning the development, the structural characterization, and the catalytic activity of piano-stool complexes including a bi- or multidentate Schiff-base ligand, *N,O-*; *N,N-*; *N,S-*; *N,O,O-*; *N,O,S*-donor, can be found in the literature [11]. Appropriate steric and electronic properties have allowed the elaboration of a wide range of stable, active and highly selective catalysts for organic reactions (hydrogenation, cyclopropanation, metathesis reactions, radical reactions, enol ester synthesis, Diels-Alder reaction, preparation of heterocycles from di-allylic compounds) [12]. In addition to their catalytic, magnetic and optical properties, piano-stool complexes incorporating Schiff-bases are of increasing interest due to their promising antibacterial and antitumoral activity [13].

Among biologically relevant piano-stool complexes, those based on

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ruthenium appear to have excellent properties, with in particular their anticancer activity, making them an alternative to cisplatin and its derivatives [14]. Thus, it has been demonstrated that water-soluble arene ruthenium Schiff-base complexes exhibited anticancer activity in vitro and in vivo, with DNA as the main cellular target [15]. It was further established that the cytotoxic activity of such complexes was influenced, not only by the nature of the hydrophobic arene ligand but also by the steric and electronic effect of the Schiff-base, whose a substitution by monodentate ligands makes the complex inactive on specific cell lines [16]. Furthermore, the presence of various heterocyclic nuclei (triazole, imidazole, thiazole, thiadiazole) in the structure of the Schiff-base has proven to have positive effects on the exaltation of anticonvulsant, antimicrobial, analgesic, antioxidant, anti-inflammatory, antifungal and anticancer properties of the Schiff-base and their corresponding metal complexes [17,18].

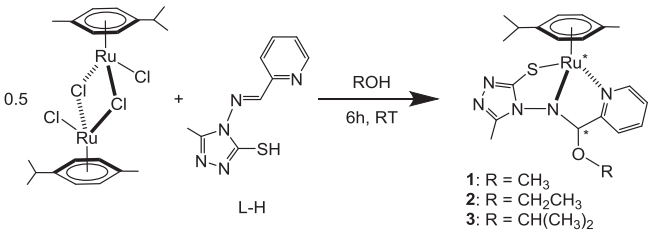
In order to promote the design of new organometallic compounds with catalytic and therapeutic potential, the present work is devoted to the synthesis and structural characterization of new arene ruthenium complexes with tridentate pyridinic Schiff-base *S,N,N*-donor ligand, containing a 1,2,4-triazole-3-thiol ring. Interestingly, a single-crystal X-ray structure analysis reveals the insertion of an alkoxy group on the carbon of the coordinated imine function, thus leading to the formation of neutral arene ruthenium complexes after reduction of the imine function. The alkoxylation reaction, concomitant with the complexation process, generates in the coordinated Schiff-base, an additional asymmetric center, which led to an original series of chiral organometallic complexes, whose enantiomers, once separated, could be used in different fields, such as asymmetric organometallic catalysts or as bioactive chiral molecules.

2. Results and discussion

The reaction at room temperature between 5-methyl-4-{(pyridin-2-ylmethylene)amino}-4H-1,2,4-triazole-3-thiol (L-H) and the dinuclear precursor $[(\eta^6\text{-MeC}_6\text{H}_4\text{Pr}^i)\text{RuCl}_2]_2$ in alcoholic solution (methanol, ethanol, isopropanol) gives a series of neutral complexes of the general formula $(\eta^6\text{-MeC}_6\text{H}_4\text{Pr}^i)\text{Ru(L-OR)}$ (R = Me, **1**; R = Et, **2**; R = Pr^i, **3**) (see Scheme 1). During the formation of the $(\eta^6\text{-MeC}_6\text{H}_4\text{Pr}^i)\text{Ru(L)}$ complex (not isolated), an alkoxylation occurs on the imine carbon of L, thus generating L-OR derivatives.

The insertion of an alkoxy group on the imine carbon atom is evidenced by ^{1}H and ^{13}C NMR spectroscopy. The azomethine proton, which is initially observed at 8.7 ppm in L-H [19], becomes significantly upfield shifted and appears between 5 and 6 ppm in the complexes (5.2 ppm in **1**, 5.8 ppm in **2**, 5.4 ppm in **3**). A similar chemical shift is observed for the corresponding carbon atom, which shifts from 164 ppm in L-H to around 100 ppm in complexes **1–3**. The reduction of the imine and insertion of the alkoxy group generates an asymmetric carbon atom on L-OR, and accordingly diastereotopic protons are observed for the adjacent O-CH_2 moiety in **2**. Indeed, two quadruplets integrating for one proton each are observed at 4.5 and 4.1 ppm respectively. The formation of L-OR and its coordination mode to the arene ruthenium unit was confirmed by the single-crystal X-ray structure analysis of complex **3**.

The molecular structure of **3** shows a piano-stool arrangement with



Scheme 1. Synthesis of the arene ruthenium complexes **1–3**.

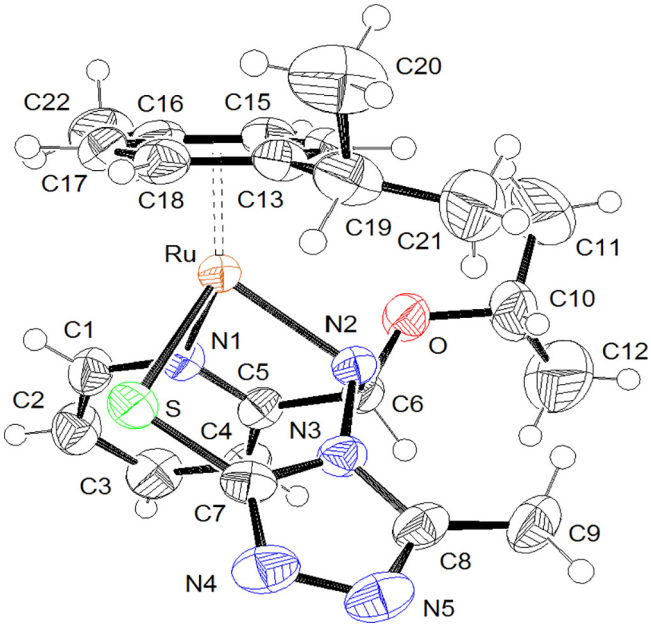


Fig. 1. Ortep drawing of **3**, at 50% probability level ellipsoids. Selected bond lengths (Å) and angles (°): Ru-S 2.3752(5), Ru-N1 2.093(2), Ru-N2 2.101(2), N2-N3 1.435(2), N4-N5 1.394(3), N2-C6 1.471(3), O-C6 1.424(2), S-C7 1.723(2), O-C10 1.430(3), Ru-centroid 1.682; S-Ru-N1 84.08(5), S-Ru-N2 86.74(4), N1-Ru-N2 79.09(7), C6-O-C10 114.73(19), N3-N2-C6 108.81(15), N2-C6-O 108.76(17), C5-C6-O 105.81(17).

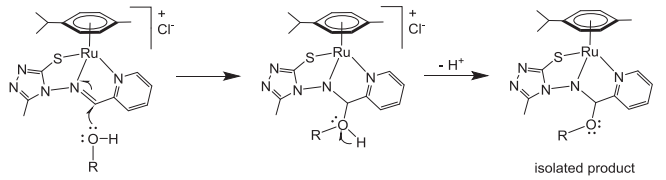
the *p*-cymene ligand, the $S_{thiolato}$, the N_{imine} and $N_{pyridyl}$ surrounding the chiral-at-metal ruthenium center. The geometrical parameters around the ruthenium center are comparable to those observed in related arene ruthenium complexes with *N,S,N*-tridentate ligands [20]. The coordination of LOR in a tridentate fashion generates asymmetry on the carbon atom (C6) located between the pyridyl ring and the N_{imine}, and accordingly the nucleophilic attack of the alkoxy group can only happen from the arene side, where it is less crowded.

As previously mentioned, the introduction of an alkoxy group on the carbon atom reduces the imine function and generates chirality on the L-OR ligand. In **3**, the *N*-C distance is 1.471(3) Å, which is in accordance with a *N*-C single bond and confirm the reduction of N = C bond. In addition, the angles around C6 are all comprised between 105.8(2) and 111.6(2)°, typical of a sp^3-hybridized carbon atom. The presence of two chiral centers can in principle generate diastereoisomers, however, only the $R_{Ru}S_C$ and $S_{Ru}R_C$ enantiomers are observed; the $S_{Ru}R_C$ enantiomer being represented in Fig. 1.

The electrospray ionization mass spectra (methanol, positive mode) of complexes **1–3** also confirm the formation of the proposed mononuclear complexes. In all cases, a cationic peak corresponding to the intact complexes with one additional proton is observed, $[M+H]^+$ (see Experimental section). The isotopic pattern of these cationic peaks correlates exactly with the calculated theoretical isotopic distributions of organometallic Ru species.

Introduction of the alkoxy group on the carbon atom of the imine function appears during the coordination process, as no such reaction is observed when L-H is dissolved in methanol or ethanol. However, at present, the exact moment of the attack remains unsure, but one can assume that the carbon atom of the imine function needs to be activated before the nucleophilic attack takes place. Therefore, we proposed a mechanism (Scheme 2) based on the assumption that the Schiff-base ligand is first coordinated to the arene ruthenium unit in a *S,N,N*-tridentate fashion.

Accordingly, upon coordination of the imine group to the ruthenium atom, the electron density of the carbon atom is reduced, thus favoring the nucleophilic attack. After formation of the C-OR bond, a H^+ is



Scheme 2. Proposed mechanism for the insertion of an alkoxy group on the imine carbon atom of L after coordination to ruthenium.

released, which generates a negative charge on the ligand. Then, the $(L\text{-}OR)^{2-}$ ligand forms a neutral complex with the $[(\eta^6\text{-}MeC_6H_4Pr^i)Ru]^{2+}$ unit. These preliminary studies suggest that primary and secondary alcohols can be introduced on L, while steric hindrance does not allow the insertion of tertiary alcohols (no alkoxylation on L in *tert*-butanol).

The stability of complex **2** in D_2O was determined over a period of 24 h. As illustrated in Fig. 2, rapid released of ethanol is observed, which is confirmed by the disappearance of the two quadruplets at 4.4 and 4.1 ppm, and the emergence of a new quadruplet at 3.7 ppm, which corresponds to free ethanol in D_2O [21]. Interestingly, new signals of the pyridyl protons are also observed during this stability experiment, suggesting new species in which a pyridyl group is coordinated (signals with similar chemical shifts to those observed for **2**), and others in which the nitrogen atom of the pyridyl group is not coordinated (new signals at for example 8.2 ppm).

To gain further insights in the decomposition process, and possibly in the overall mechanism, the D_2O solution after the 24 h period was analyzed by mass spectrometry under different conditions (positive and negative modes, see the Supplementary Data). The aqueous solution contains, among others, the following organic fragments, ethanol, 4-amino-5-methyl-1,2,4-triazole-3-thiol, 2-pyridine-carboxamide, and 2-pyridinecarboxaldehyde (Fig. 3). These organic fragments are the starting materials for the synthesis of L-H and accordingly the decomposition products of LOR. Therefore, we can assume that the formation of the $(\eta^6\text{-}MeC_6H_4Pr^i)Ru(L\text{-}OR)$ complexes corresponds to the isolated form of the first intermediate in the hydrolysis of Schiff-base ligands.

3. Conclusion

Reactions in alcoholic solutions between *p*-cymene ruthenium complexes and the functionalized Schiff-base 5-methyl-4-{(pyridin-2-ylmethylene)amino}-4H-1,2,4-triazole-3-thiol have showed an alkoxylation of the imine carbon atom of the Schiff-base by primary and secondary alcohols. The insertion of the OR group reduces the imine function, which overall diminishes the stability of the coordinated L-OR ligand. Coordination of the Schiff-base in a *S,N,N*-tridentate fashion as well as the alkoxylation generate two chiral centers in the complexes,

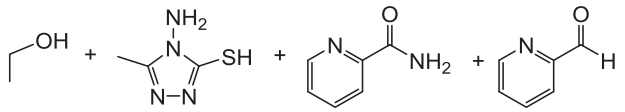


Fig. 3. Organic fragments observed by ESI-MS from the aqueous solution of **2** (D_2O, 24 h, room temperature).

but only one pair of enantiomers. These new arene ruthenium complexes are quite interesting in terms of reactivity, and further investigation will be needed to fully understand the alkoxylation mechanism, and to determine their potentials as catalysts and as therapeutic agents.

4. Experimental section

4.1. Materials and methods

All chemicals were purchased from commercial sources and used as received unless specified otherwise. The starting materials $[(\eta^6\text{-}MeC_6H_4Pr^i)RuCl_2]_2$ [22] and 5-methyl-4-{(pyridin-2-ylmethylene) amino}-4H-1,2,4-triazole-3-thiol (L-H) [19] were prepared according to published methods. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Avance II 400 spectrometer using the residual protonated solvent as internal standard. Infrared spectra were recorded on a Thermo Scientific iS5 ATR/FTIR spectrometer. Electrospray ionisation mass spectra were obtained in positive ion mode on a Bruker FTMS 4.7 T BioAPEX II mass spectrometer, University of Fribourg (Switzerland). UV-visible absorption spectra were recorded in methanol on a Perkin Elmer UV/Vis spectrophotometer at 10^{-5} M concentrations.

4.2. General synthesis of the complexes $(\eta^6\text{-}MeC_6H_4Pr^i)Ru(L\text{-}OR)$ (1–3)

The metal precursor $[(\eta^6\text{-}MeC_6H_4Pr^i)RuCl_2]_2$ (50 mg; 0.082 mmol) and 2 equivalents of L-H (36 mg; 0.164 mmol) were dissolved in dry alcohol (methanol for **1**, ethanol for **2** and isopropanol for **3**) (15 mL) and stirred at room temperature for 6 h. After removing the solvent, the precipitate was purified by column chromatography on silica gel, using a mixture of methanol/ethyl acetate/hexane as eluent (**1**:6/3/3; **2**:6/3/1; **3**:4/2/3), and the isolated solid was dried under vacuum.

1: Orange solid, Yield: 20 mg, 0.041 mmol (50.3%). ^1H NMR (400 MHz, MeOD) δ (ppm); 8.73 (d, 1H, J = 5.2 Hz, C**H**$_{pyr}$), 7.82 (t, 1H, J = 7.6 Hz, C**H**$_{pyr}$), 7.51 (d, 1H, J = 7.5 Hz, C**H**$_{pyr}$), 7.39 (t, 1H, J = 6.4 Hz, C**H**$_{py}$), 5.67 (d, 1H, J = 5.3 Hz, C**H**$_{p\text{-}cym}$), 5.63 (d, 1H, J = 5.7 Hz, C**H**$_{p\text{-}cym}$), 5.57 (d, 1H, J = 5.7 Hz, C**H**$_{p\text{-}cym}$), 5.49 (d, 1H, J = 5.7 Hz, C**H**$_{p\text{-}cym}$), 5.20 (s, 1H, NC**H**), 3.84 (s, 3H, OC**H**$_3$), 2.78 (sept, 1H, J = 6.7 Hz, C**H**$(CH_3)_2$), 2.48 (s, 3H, C**H**$_3$), 2.00 (s, 3H, C**H**$_3$), 1.20

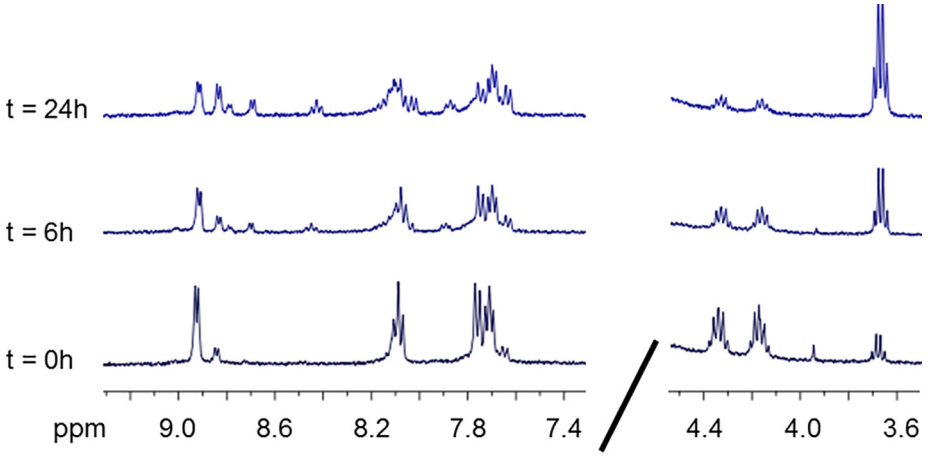


Fig. 2. Stability of complex **2** in D_2O at room temperature over a period of 24 h.

Table 1
Crystallographic and structure refinement parameters of complex **3**.

	3
Chemical formula	$C_{22}H_{29}N_5ORuS$
Formula weight	512.63
Crystal system	monoclinic
Space group	*P* $2_1/n$ (no. 14)
Crystal color & shape	orange block
Crystal size	0.21 × 0.20 × 0.17
a (Å)	14.3899(8)
b (Å)	10.4287(4)
c (Å)	15.8989(8)
β (°)	101.480(4)
V (Å^3)	2338.2(2)
Z	4
T (K)	293(2)
D_c (g.cm^{-3})	1.456
μ (mm^{-1})	0.782
Scan range (°)	1.74 < θ < 29.21
Unique reflections	6331
Reflections used [I > 2σ(I)]	4984
R_{int}	0.0540
Final R indices [I > 2σ(I)]*	0.0311, wR_2 0.0678
R indices (all data)	0.0464, wR_2 0.0718
Goodness-of-fit	0.984
Max, Min Δρ/e (Å^{-3})	0.515, −0.710

* Structures were refined on F_0^2: wR_2 = $[\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma w(F_0^2)^2]^{1/2}$, where $w^{-1} = [\Sigma(F_0^2) + (aP)^2 + bP]$ and $P = [\max(F_0^2, 0) + 2F_c^2]/3$.

(d, 3H, *J* = 6.7 Hz, CH(C**H**$_3$)$_2$), 1.09 (d, 3H, *J* = 6.7 Hz, CH(C**H**$_3$)$_2$). ^{13}C{^{1}H} NMR (101 MHz, MeOD) δ (ppm); 164.9 (S-**C** = N), 163.4 (OCH**C**), 154.1 (**C**H$_{pyr}$), 147.4 (C**C** = N), 138.3 (**C**H$_{pyr}$), 125.4 (**C**H$_{pyr}$), 122.7 (**C**H$_{pyr}$), 104.7 (**C**CH$_3$), 104.6 (O**C**HC), 100.2 (**C**CH(CH$_3$)$_2$), 86.0 (**C**H$_{p\text{-cym}}$), 85.0 (**C**H$_{p\text{-cym}}$), 84.4 (**C**H$_{p\text{-cym}}$), 55.0 (OCH$_3$), 30.8 (C**C**H(CH$_3$)$_2$), 22.5 (CCH(**C**H$_3$)$_2$), 20.0 (CCH(**C**H$_3$)$_2$), 16.8 (C**C**H$_3$), 9.8 (C**C**H$_3$). IR: υ (cm^{-1}): 3350.1 (w, CH$_{p\text{-cym}}$), 2966.4 (w, CH), 1415.1 (s, C = C), 1281.2 (m, *N-N*), 1094.3 (s, C-O). UV–visible: (1.0 × 10^{-5} M, MeOH, 298 K): λ_{max} 359 nm (ε = 19000 M^{-1}·cm^{-1}), 639 nm (ε = 4900 M^{-1}·cm^{-1}). ESI-MS (MeOH): *m/z* = 486.1 [M + H]$^+$.

2: Dark green solid, Yield: 32 mg, 0.064 mmol (78.0%). ^{1}H NMR (400 MHz, MeOD) δ (ppm); 8.90 (d, 1H, *J* = 5.1 Hz, C**H**$_{pyr}$), 8.04 (t, 1H, *J* = 7.4 Hz, C**H**$_{pyr}$), 7.76 (d, 1H, *J* = 7.1 Hz, C**H**$_{pyr}$), 7.63 (d, 1H, *J* = 6.2 Hz, C**H**$_{pyr}$), 5.93 (s, 2H, C**H**$_{p\text{-cym}}$), 5.88 (s, 1H, C**H**$_{p\text{-cym}}$), 5.78 (d, 2H, *J* = 5.2 Hz, C**H**$_{p\text{-cym}}$, NC**H**), 4.53 (q, 1H, *J* = 7.4 Hz, OC**H**$_2$CH$_3$), 4.09 (q, 1H, *J* = 7.4 Hz, OC**H**$_2$CH$_3$), 2.83 (sept, 1H, *J* = 7.0 Hz, C**H**(CH$_3$)$_2$), 2.67 (s, 3H, C**H**$_3$), 2.06 (s, 3H, C**H**$_3$), 1.46 (t, 3H, *J* = 7.0 Hz, OCH$_2$C**H**$_3$), 1.25 (d, 3H, *J* = 7.0 Hz, CH(C**H**$_3$)$_2$), 1.12 (d, 3H, *J* = 6.8 Hz, CH(C**H**$_3$)$_2$). ^{13}C{^{1}H} NMR (101 MHz, MeOD) δ (ppm); 165.1 (S**C** = N), 155.2 (**C**H$_{pyr}$), 147.6 (C**C** = N), 146.8 (OCH**C**), 139.8 (**C**H$_{pyr}$), 127.3 (**C**H$_{pyr}$), 123.9 (**C**H$_{pyr}$), 103.0 (**C**CH$_3$), 101.4 (N**C**H), 86.0 (**C**H$_{p\text{-cym}}$), 84.8 (**C**H$_{p\text{-cym}}$), 84.2 (O**C**HC), 67.7 (**C**H$_2$CH$_3$), 30.8 (C**C**H(CH$_3$)$_2$), 22.5 (CCH(**C**H$_3$)$_2$), 19.7 (CCH(**C**H$_3$)$_2$), 16.5 (N = C**C**H$_3$). 13.7 (CH$_2$**C**H$_3$), 13.8 (C**C**H$_3$). IR: υ (cm^{-1}): 3379.5 (w, CH$_{p\text{-cym}}$), 2965.6 (w, CH), 1423.9 (s, C = C), 1285.3 (m, *N-N*), 1095.4 (s, C-O). UV-visible: (1.0 × 10^{-5} M, MeOH, 298 K): λ_{max} 450 nm (ε = 8900 M^{-1}·cm^{-1}), 639 nm (ε = 5200 M^{-1}·cm^{-1}). ESI-MS (MeOH): *m/z* = 500.1 [M + H]$^+$.

3: Brown solid, Yield: 28 mg, 0.054 mmol (66.6%). ^{1}H NMR (400 MHz, MeOD) δ (ppm); 8.72 (d, 1H, *J* = 5.0 Hz, C**H**$_{pyr}$), 7.83 (t, 1H, *J* = 7.4 Hz, C**H**$_{pyr}$), 7.48 (d, 1H, *J* = 7.6 Hz, C**H**$_{pyr}$), 7.39 (t, 1H, *J* = 6.1 Hz, C**H**$_{pyr}$), 5.68 (d, 1H, *J* = 5.4 Hz, C**H**$_{p\text{-cym}}$), 5.63 (s, 2H, C**H**$_{p\text{-cym}}$) 5.50 (d, 1H, *J* = 5.7 Hz, C**H**$_{p\text{-cym}}$), 5.37 (s, 1H, NC**H**), 4.59–4.48 (m, 1H, C**H**(CH$_3$)$_2$), 2.87–2.69 (m, 1H, C**H**(CH$_3$)$_2$), 2.48 (s, 3H, C**H**$_3$), 2.01 (s, 3H, C**H**$_3$), 1.46 (d, 3H, *J* = 5.9 Hz, CH(C**H**$_3$)$_2$), 1.37 (d, 3H, *J* = 5.7 Hz, CH(C**H**$_3$)$_2$), 1.20 (d, 3H, *J* = 6.8 Hz, CH(C**H**$_3$)$_2$), 1.09 (d, 3H, *J* = 6.7 Hz, CH(C**H**$_3$)$_2$). ^{13}C{^{1}H} NMR (101 MHz, MeOD) δ (ppm); 164.9 (S**C** = N), 164.0 (C**C** = N), 154.1 (**C**H$_{pyr}$), 147.4 (OCH**C**), 138.4 (**C**H$_{pyr}$), 125.2 (**C**H$_{pyr}$), 122.2 (**C**H$_{pyr}$), 104.5 (**C**H$_{pyr}$), 101.4 (N**C**H), 99.7 (**C**CH(CH$_3$)$_2$), 86.0 ((**C**CH$_3$)$_{p\text{-cym}}$), 85.4 (**C**H$_{p\text{-cym}}$), 84.7 (**C**H$_{p\text{-cym}}$), 84.2 (**C**H$_{p\text{-cym}}$), 69.7 (O**C**H(CH$_3$)$_2$), 30.8 (**C**H(CH$_3$)$_2$), 22.7 (CH(**C**H$_3$)$_2$), 22.6 (CH(**C**H$_3$)$_2$), 21.3 (OCH(**C**H$_3$)$_2$), 20.0 (OCH(**C**H$_3$)$_2$), 16.8 (**C**H$_3$), 9.6 (**C**H$_3$). IR: υ (cm^{-1}): 3064.8 (w, CH$_{p\text{-cym}}$), 2961.3 (w, CH), 1417.5 (s, C = C), 1277.7 (m, *N-N*), 1030.2 (s, C-O). UV–visible: (1.0 × 10^{-5} M, MeOH, 298 K): λ_{max} 259 nm (ε = 22,000 M^{-1}·cm^{-1}), 652 nm (ε = 6300 M^{-1}·cm^{-1}). ESI-MS (MeOH): *m/z* = 514.1 [M + H]$^+$.

4.3. X-ray diffraction analysis

Crystals of **3** were obtained by the slow diffusion of pentane in a methanol solution of **3**. A crystal of **3** was mounted on a Stoe Image Plate Diffraction system equipped with a *ϕ* circle goniometer, using Mo-Kα graphite monochromated radiation (λ = 0.71073 Å) with *ϕ* range 0–200°. The structure was solved by direct methods using the program SHELXS-97, while the refinement and all further calculations were carried out using SHELXL-97 [23]. The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters, while the non-H atoms were refined anisotropically using weighted full-matrix least-square on F^2. Crystallographic details are summarized in Table 1. Fig. 1 was drawn with ORTEP [24].

CCDC-1840701 complex **3** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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Appendix A. Supplementary data

Mass spectrometry spectra (positive and negative mode) of the decomposition products obtained from complex **2**.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.ica.2018.07.025.

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