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Influence of substituted pyridines in the chemical behavior of dimethyl sulfoxide ruthenium complexes

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ABSTRACT

$[RuCl_2(S–DMSO)_2(X–py)_2]$ type complexes, with X = H (**1**), 4-$CONH_2$ (**2**), or 3-$CONH_2$ (**3**), exhibited *trans*,-*cis*,*cis* conformational isomer (species **A**), with additional *cis*,*cis*,*cis* isomer type (species **B**) for **1**. Electronic spectra with bands in the wavelength range of 270–450 nm were unchanged for 120 min at 25 °C in CH_3CN. Irradiation at 350 nm provided replacement of DMSO ligands by CH_3CN solvent molecules. Cyclic voltammetry studies in CH_3CN revealed an electrochemical–chemical process with a Ru–(S–DMSO) to Ru–(O–DMSO) linkage isomerization for species **B** from **1**. The complexes were inactive for the ring-opening metathesis polymerization (ROMP) of norbornene (NBE) for 60 min at 25 °C. However, polyNBE was produced by aging the complex solutions for 90–200 min at 25 °C, raising the temperature to 50 °C, irradiating the solutions at 350 nm for 5–10 min or when the complexes were in the presence of NBu_4ClO_4.

1. Introduction

Dimethyl sulfoxide (DMSO) presents a selective affinity for different electronic population in Ru–DMSO complexes. It is a S-bonded molecule (S–DMSO) for Ru^{II} d^6 low spin configuration and an O-bonded molecule (O–DMSO) for Ru^{III} d^5 low spin configuration [1–4]. DMSO is classified as a versatile molecule for the development of Ru-based initiators for a variety of catalytic reactions because of its ambidentate behavior. For example, hydrogen-atom transfer [5–7], hydrogenation [8], R-alkylation of ketones [9], aerobic oxidation of alcohols [10], oxidation of aliphatic ethers to esters [11], isomerization of alcohols [12], selective oxidation of aryl sulfides with molecular oxygen [13,14] and nitrile hydration [15] were already investigated. In particular, ring-opening metathesis polymerization (ROMP; Scheme 1) of cyclic olefins with *fac*-$[RuCl_2(S–DMSO)_3(O–DMSO)]$ complex produced polyNBE with 62% yield and PDI of *ca.* 1.6 for 5 min at room temperature [16]. DMSO molecules worked as ancillary ligands and the S-/O-bonded exchange explain the Ru catalytic behavior. However, no polymer was obtained under a variety of conditions when introducing σ-donor imidazole type ligands in the coordination sphere of the Ru–DMSO type complex [16], where the S–DMSO was strongly coordinated, deactivating the initiator. This was contrary to the case of Ru–DMSO type complex with σ-donor PCy_3 ligand [17] where the DMSO molecules were discoordinated in the induction period to start the catalytic cycle due to phosphine steric hindrance. In the latter case, DMSO had no effect on the catalytic reaction itself.

From these examples, a further idea is to introduce moderate σ-donor/π-acceptor ligands in Ru–DMSO complexes to provoke a latent behavior that could be ceased by external action. An inert or partially active complex can be triggered by an external stimulus, such as light, temperature or salt [18–20]. For instance, immediate quantitative yield was obtained by *fac*-$[RuCl_2(S–DMSO)_3(O–DMSO)]$ complex when in presence of NBu_4ClO_4 at room temperature [16]. In the case of inert complex, such initiators are of particular interest in technical applications because they enable the premixing of a monomer/initiator mixture and its storage over a longer period, which can be proceeded even at elevated temperatures [18–20]. The coordination sphere of Ru–DMSO can be manipulated to be a viable option of latent ROMP initiators, considering their quite elevated resistance to humidity and air. The development of robust initiators that could be stored, handled and capable of working without restriction to air, moisture, light and warmth can be a cheaper alternative for industrial processes [21].

Considering the lack of reports on pyridine–Ru–DMSO type complexes, we investigated the influence of the $CONH_2$ substituent in positions 3 and 4 of the pyridine ring (Fig. 1), taking into account

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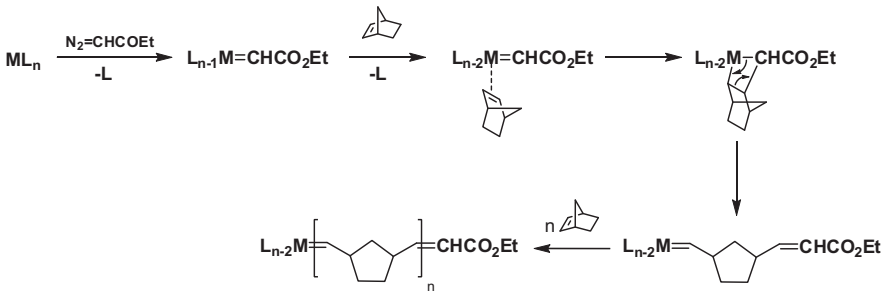

Scheme 1. Illustration of a general mechanism to a typical ROMP reaction.

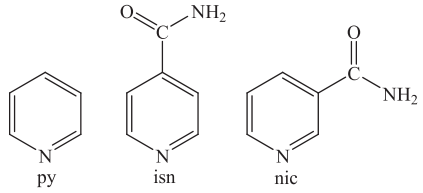

Fig. 1. Pyridine (py), isonicotinamide (isn) and nicotinamide (nic) chemical structures.

the electronic character compared with the pyridine itself (X = H; pK_a = 5.2): isonicotinamide (isn; X = 4-$CONH_2$; pK_a = 3.5) and nicotinamide (nic; 3-$CONH_2$; pK_a = 3.4). Substituted-pyridines (X–py) could manipulate the ROMP efficiency when increasing or decreasing the electronic population in Ru–DMSO type complexes, observing the existence of S- or O-bonded molecules. Development of successful initiators for ROMP by combing ancillary ligands in Ru complexes has been achieved, where homopolymers and copolymers have been obtained with improved thermal properties [22,23]. Cyclic voltammetric and photochemical studies were performed to observe the chemical behavior of the complexes in solution. ROMP reactions of NBE were carried out to verify the complex activation by aging the complex solution, raising the reaction temperature, irradiating with light, or in the presence of NBu_4ClO_4.

2. Experimental

2.1. General remarks

All the solvents were of analytical grade and were distilled from the appropriate drying agents immediately prior to use. $RuCl_3{\cdot}xH_2O$, norbornene (NBE), pyridine (py), nicotinamide (nic), isonicotinamide (isn), tetrabutylammonium hexafluorophosphate ($TBAPF_6$) and ethyldiazoacetate (EDA) from Aldrich and dimethylsulfoxide (DMSO) from Merck were used as acquired. *fac*-[$RuCl_2$(S–DMSO)$_3$(O–DMSO)] was prepared according to literature procedures [24]. All manipulations were performed under argon atmosphere (99.9%). Room temperature (r.t.) was 23 ± 1 °C.

2.2. Synthesis of [$RuCl_2$(S–DMSO)$_2$(py)$_2$] (**1**)

This was obtained from modified literature procedure [25]. A 0.18 mL (2.2 mmol) sample of pyridine and 400 mg (0.82 mmol) of *fac*-[$RuCl_2$(S–DMSO)$_3$(O–DMSO)] were dissolved in 20 mL of $CHCl_3$, and the resulting solution was refluxed for 1 h. The solvent volume was reduced to *ca.* 5 mL and 10 mL of diethyl ether was added at r.t. A yellow precipitate was filtered, washed with cold diethyl ether and dried in vacuum (yellow; 367 mg, 92% yield). *Anal.* Calc. for $C_{14}H_{22}Cl_2N_2O_2RuS_2$ (M_w 485.46): C, 34.50; H, 4.76; N, 5.75. Found: C, 34.54; H, 4.58; N, 5.62%. FTIR (CsI, cm^{-1}): 1093, 1076 ($\nu_{S=O}$), 424 (ν_{Ru-S}), 350, 310, 277 (ν_{Ru-Cl}). ^{1}H NMR ($CDCl_3$, δ): species **A** – *tcc*, 9.09 ppm (*ortho*-H, py); 7.27 ppm (*meta*-H, py) and 7.76 (*para*-H, py), 3.21 (12H, s, CH_3, S–DMSO); species **B** – *ccc*, 8.74 ppm (*ortho*-H, py), 7.13 ppm (*meta*-H, py), 7.62 ppm (*para*-H, py), 3.65, 3.36, 2.79 and 2.67 (CH_3, S–DMSO).

2.3. Synthesis of new [$RuCl_2$(S–DMSO)$_2$(isn)$_2$] (**2**) and [$RuCl_2$(S–DMSO)$_2$(nic)$_2$] (**3**)

A 402 mg (3.3 mmol) sample of amine (isn or nic) was added to the solution of *fac*-[$RuCl_2$(S–DMSO)$_3$(O–DMSO)] (0.82 mmol; 400 mg) in acetone/$CHCl_3$ mixture (1:1, 40 mL). The resulting solution was refluxed for 1 h. The complexes precipitated when the volumes of the solutions were reduced to *ca.* 5 mL in vacuum. The solids were filtered, washed with diethyl ether and vacuum-dried. [$RuCl_2$(S–DMSO)$_2$(isn)$_2$] – *Anal.* Calc. for $C_{16}H_{24}Cl_2N_4O_4RuS_2$ (M_w 573.50) (yellow; 352 mg, 75% yield): C, 33.51; H, 4.39; N, 9.77. Found: C, 33.50; H, 4.50; N, 9.80%. FTIR (CsI, cm^{-1}): 1065, 1050 ($\nu_{S=O}$), 424 (ν_{Ru-S}), 355 (ν_{Ru-Cl}). ^{1}H NMR (DMSO-d_6, 200 MHz; δ): 8.97 and 8.64 ppm (*ortho*-H, isn), 7.71–7.63 ppm (*meta*-H, isn), 8.24 and 7.77 ppm (NH_2, isn), 3.14 ppm (CH_3, S–DMSO). [$RuCl_2$(S–DMSO)$_2$(nic)$_2$] – *Anal.* Calc. for $C_{16}H_{24}Cl_2N_4O_4RuS_2$ (M_w 573.50) (yellow; 375 mg, 80% yield): C, 33.51; H, 4.39; N, 9.77. Found: C, 33.34; H, 4.43; N, 9.72%. FTIR (CsI, cm^{-1}): 1087, 1070 ($\nu_{S=O}$), 421 (ν_{Ru-S}), 349 (ν_{Ru-Cl}). ^{1}H NMR (DMSO-d_6, 200 MHz; δ): 9.38 and 9.00 ppm (*ortho*-H, nic), 8.24 ppm (*para*-H, nic), 7.45–7.36 ppm (*meta*-H, nic), 8.07 and 7.59 ppm (NH_2, nic), 3.13 (CH_3, S–DMSO).

2.4. Instrumentation

Elemental analyses were performed in a Perkin–Elmer CHN 2400 in the Elemental Analysis Laboratory at Institute of Chemistry – USP. ESR measurements from solid sample were carried out at 77 K using a Bruker ESR 300C apparatus (X-band) equipped with a TE102 cavity and HP 52152A frequency counter. FTIR spectra were obtained in CsI pellets on a Bomem FTIR MB 102. Electronic spectra were recorded on a Varian model Cary 500 NIR spectrophotometer, using 1 cm path length quartz cells. The NMR (^{1}H; ^{13}C{^{1}H}; ^{31}P{^{1}H}) spectra were obtained in DMSO-d_6 at 25.0 ± 0.1 °C using a Bruker AC-200 spectrometer. Size exclusion chromatography (SEC) analyses were carried out on a Shimadzu Prominence LC system equipped with a LC-20AD pump, a DGU-20A5 degasser, a CBM-20A communication module, a CTO-20A oven at 27 °C and a RID-10A detector, connected with three PL gel columns (5 μm MIXED-C: 30 cm, Ø = 7.5 mm). The retention time was calibrated with standard monodispersed polystyrene using HPLC-grade $CHCl_3$ as eluent. Polydispersity index (PDI) is M_w/M_n. Cyclic voltammetry measurements were performed on a μAutolab Type III potentiostat with a stationary platinum disk and a wire as working and auxiliary electrodes, respectively. The reference electrode was Ag/AgCl. The measurements were at 25 °C ± 0.1 in CH_3CN with 0.1 $mol_x\,L^{-1}$ of $TBAPF_6$. The $E_{1/2}$ values