**Supplementary Material**

*cis*-fac-dichlorotetrakis(dimethylsulfoxide)ruthenium(II) precursor and different oximes as sources of nitrosyl ligand

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**S3.4 Determination of Kinetic and Thermodynamic Parameters of the Thermal Decomposition**

The Horowitz and Metzger equation, Cs = (n)1/1-n, where Cs is the weight fraction of the substance present at the DTG peak temperature Ts, is given as:

Cs =  Eq. S1

and was used for the determination of the values of the reaction order (n). Here Ws stands for the remaining weight of the substance at a given temperature Ts, *i.e.*, the DTG peak temperature, Wi and Wf are the initial and final weights of the substance, respectively. The values of Cs for the thermal decomposition of complexes are not in the range 0.30–0.39, which indicate that the decomposition is not first-order kinetics [S1]. For a first order and not first order process the Horowitz and Metzger equations may be written in the form:

 *n* =1 Eq. S2

 *n* ≠1 Eq. S3

where α is the fraction decomposition at time t and is given by:

 Eq. S4

(mo is the mass at the beginning of the decomposition steps, mt is the mass at time t, mf is the mass at the end of the decomposition steps).

R is the gas constant (8.314 JK-1 mol-1), Ea is the activation energy in J mol−1, θ (T−Ts) K.

φ is the heating rate and Ts temperature at DTG peak. A is Arrhenius constant (sec−1).

The kinetic parameters were calculated from the plots of the left-hand side of Eqs. (S2) and (S3) with θ.

The correlation coefficient r (0.95-0.99) is computed using the least-square method for Eqs. (S2) and (S3). The Ea values were calculated from the slope of the decomposition step curve and the Avalue was determined from the intercept.

The activation entropy ΔS\*, the activation enthalpy ΔH\* and the free energy of activation ΔG\* were calculated using the following equations [S2-S4].

 Eq. S5

ΔH\* = Ea − nRT Eq. S6

ΔG\* = ΔH\*− Ts ΔS\* Eq. S7

K = Boltzmann constant (1.3086× 10−23), h = Plank constant (6.626× 10−34).

**References**

[S1] H.H. Horowitz, G. Metzger. *Anal. Chem.*, **35**, 1464 (1963).

[S2] R.H. Abu-Eittah, N.G. Zaki, M.M.A. Mohamed, L.T. Kamel. *J. Anal. Appl. Pyrolysis*, **77**, 1 (2006).

[S3] **C.J. Marmion**, T. Murphy, J.R. Docherty, K.B. Nolan. Chem. Commun., **13,** 1153 **(**2000).

# [S4] R. Mahfouz, E. Al-Frag, M.R.H. Siddiqui, W.Z. Al-kiali, O. Karama. *Arab. J. Chem.*, 4, 119 (2011).

Table S1. The weight in grams and the corresponding molar ratio for the metal precursor, *cis*-[RuCl2(DMSO)4], **P**, and the used ligands, benzohydroxamic acid (BHA), **1'**, anti-diphenylglyoxime (H2dpg), **2'**, and dimethylglyoxime (H2dmg), **3'**.

|  |  |  |
| --- | --- | --- |
| Complexes | Precursor gm (mmol) | Used Ligand/gm (mmol) |
| 1  **2**  **3** | 0.100(1)  0.100(1)  0.100(1) | 0.054 (2)  0.097 (2)  0.047 (2) |

Table S2. Some analytical data of complexes.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| *Complex* | *Molecular formula* | *F. Wt M.W* | *M. p oC* | *Color* | *Elemental analysis*  *(found) calc.%* | | | Λm  (Ohm−1cm2mol−1) |
| *C H N* | | |
| **P**  **1**  **2**  **3** | C8H24S4O4Cl2Ru  C13H24NS3O5Cl2Ru  C20H30N3S3O6Cl2Ru  C10H25N3S3O6Cl2Ru | 484  572  676  551 | 190  95  140  150 | Yellow  Dark  brown  Brown  Yellowish  brown | (19.8)  19.8  (28.1)  27.2  (40.0)  39.4  (24.0)  21.7 | (4.9)  4.9  (3.5)  4.2  (4.0)  4.4  (4.7)  4.5 | −  (4.0)  4.9  (6.9)  6.2  (9.0)  7.6 | 67.5  75.1  68.2  66.6 |

Table S3. FT-IR spectral data of the ligands and complexes.

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| *Complexes*  *and*  *Compounds\** | ν  (N≡O) | ν  (SOS-bonded) | ν  (SOO-bonded) | ν  (C=O) | ν  ( C=N,  C-N) | ν  (OH) | ν  (NH) | ν  (Ru-NNitrosyl) | ν  Ru−O | ν  Ru−S |  |
| **P**  **1''**  **1**  **2''**  **2**  **3''**  **3** | -  -  1846 s  -  1869 s  -  1878 m | 1095, 1122s  -  1096s  -  1086s  -  1073 s | 920m  -  919m  -  886w  -  - | -  1646s  1638m  -  -  -  - | -  1560s  1476w  1629m  1623m  1690w  1639w | -  2750br  -  3270s  3153m  3207s  1630w | -  3295s  3232br  -  -  -  - | -  -  693m  -  690m  -  678m | 477w  -  474w  -  513w  -  - | 425m  -  424m  -  425m  -  436m |  |

\* s = strong, m = medium, w = weak, br = broad

Table S4. 1H NMR spectral data (δ, ppm) of the ligands and complexes.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| *Complexes and*  *Compounds* | CH3  (DMSO-S) | CH3  (DMSO-O) | H(NH) | H(OH) | H(aromatic) | H(aliphatic) |
| **P**  **1''**  **1**  **2''**  **2**  **3''**  **3** | 3.53-3.20 (18H)  -  3.30-3.50 (12H)  -  3.20-3.46 (12H)  -  3.10-3.39 (18H) | 2.74 (6H)  -  2.60 (6H)  -  2.54 (6H)  -  - | -  11.20 (1H)  13.50 (1H)  -  -  -  - | -  9.27 (1H)  -  11.60 (2H)  12.00 (1H)  11.30 (2H)  13.10 (1H) | -  7.40-7.70 (5H)  7.40-8.00 (5H)  7.44 (10H)  7.10-7.70 (10H)  -  - | -  -  -  -  -  1.89 (6H)  1.90-2.10 (6H) |

Table S5. The electronic data of complexes **P**, **1**, **2** and **3**.

|  |  |  |
| --- | --- | --- |
| *Complex* | λmax, nm (ε, L mol−1 cm−1) | Assignment |
| **P**  **1**  **2**  **3** | 260 (53300), 313 (2400), 360 (3100)  250 (89200), 280 (28000), 320 (1000)  248 (94100), 260 (90800), 448 (22500)  247 (78400), 258 (72900), 370 (71600) | π→π\*, dπ→π\* (MLCT).  π→π\*, dπ→π\* (MLCT).  π→π\*, dπ→π\* (MLCT).  π→π\*, dπ→π\* (MLCT). |

2400

4000

3600

3200

2800

2400

2000

1800

1600

1400

1200

1000

800

600

400.0

**cm-1**

%T

2998.00

2917.83

1431.45

1404.44

1308.49

**1108.19**

**1095.9**

1019.70

984.26

974.26

946.89

**920.85**

711.54

676.64

**477.33**

**425.66**

Figure S1.TheFT-IR spectrum of the investigated complex **1**.

4400.0

4000

3600

3200

2800

2400

2000

1800

1600

1400

1200

1000

800

600

400.0

**cm-1**

**%T**

**3153.76**

3056.67

2919.35

**1869.80**

**1623.99**

1376.25

1309.75

1266.38

1180.41

1159.53

**1086.47**

1015.76

969.26

908.81

**886.42**

768.82

747.88

730.42

**690.48**

607.15

**513.36**

**425.93**

Figure S2.TheFT-IR spectrum of the investigated complex **2**.

4000.0

3600

3200

2800

2400

2000

1800

1600

1400

1200

1000

800

600

400.0

**cm-1**

**%T**

3433.03

**3221.05**

3002.66

2917.93

2746.38

**1878.51**

**1437.91**

1348.63

1320.02

1192.50

1146.57

**1073.78**

**1042.32**

1016.36

970.05

712.74

**678.61**

619.09

**443.97**

**436.28**

**1630.02**

Figure S3.TheFT-IR spectrum of the investigated complex **3**.

2400

4000

3600

3200

2800

2400

2000

1800

1600

1400

1200

1000

800

600

400.0

**cm-1**

%T

2998.00

2917.83

1431.45

1404.44

1308.49

**1108.19**

**1095.9**

1019.70

984.26

974.26

946.89

**920.85**

711.54

676.64

**477.33**

**425.66**

Figure S4.TheFT-IR spectrum of the precursor complex **P**.

4000

3600

3200

2800

2400

2000

1800

1600

1400

1200

1000

800

600

400.0

**cm**-1

%T

**3295.32**

3061.45

**2750.76**

**1646.98**

1560.43

1490.57

1315.63

1163.53

1077.67

1040.40

1022.56

**898.23**

797.05

706.08

690.25

**518.02**

**429.11**

Figure S5.TheFT-IR spectrum of the precursor complex **1'**.

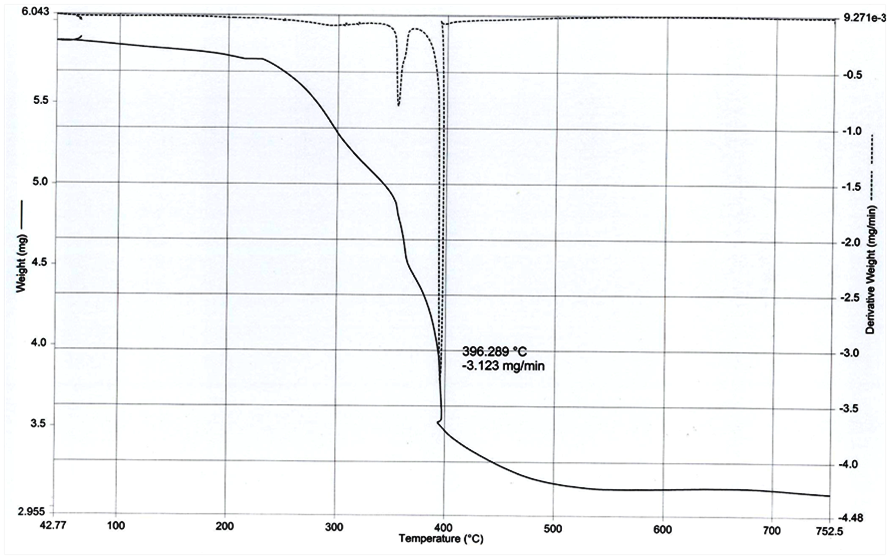


Figure S6.Typical TG/DTG curves of complex **1**.

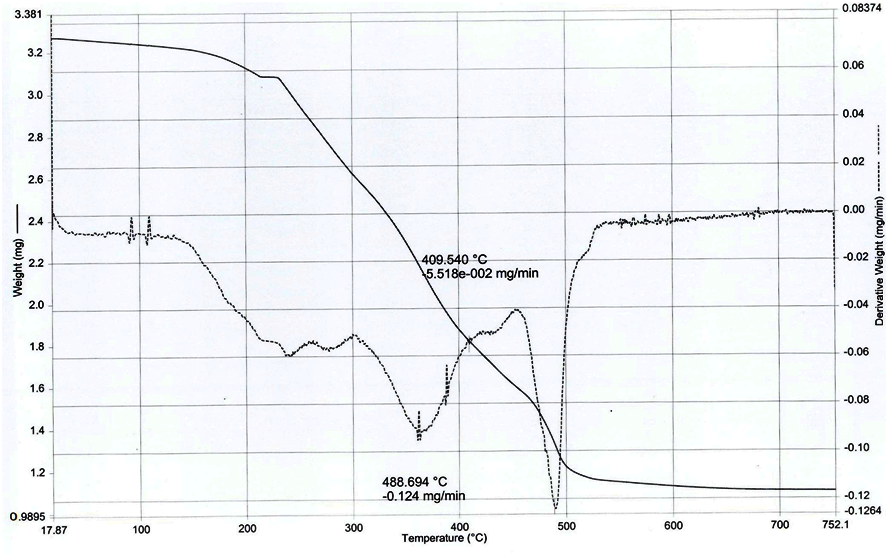


Figure S7.Typical TG/DTG curves of complex **2**.

4400.0

4000

3600

3200

2800

2400

2000

1800

1600

1400

1200

1000

800

600

400.0

**cm-1**

**%T**

1140.25

621.40

Figure S8.TheFT-IR spectrum of RuO2.