Supporting information for

Rhodium(III) and ruthenium(II) complexes of redox-active, chelating N-heterocyclic carbene/thioether ligands

Agnès Labande,*[a] Jean-Claude Daran,[a] Nicholas J. Long,*[b] Andrew J. P. White[b] and Rinaldo Poli[a,c]

[a] *CNRS ; LCC (Laboratoire de Chimie de Coordination) ; 205, route de Narbonne, F-31077 Toulouse, France, and Université de Toulouse ; UPS, INPT ; LCC ; F-31077 Toulouse, France. Fax: +33561553003; Tel: +33561333158; E-mail: agnes.labande@☺lcc-toulouse.fr.*
[b] *Department of Chemistry, Imperial College London, London, SW7 2AZ, United Kingdom. Fax: +44 2075945804; Tel: +44 2075945781; E-mail: n.long@imperial.ac.uk.*
[c] *Institut Universitaire de France, 103, bd Saint-Michel, 75005 Paris, France.*

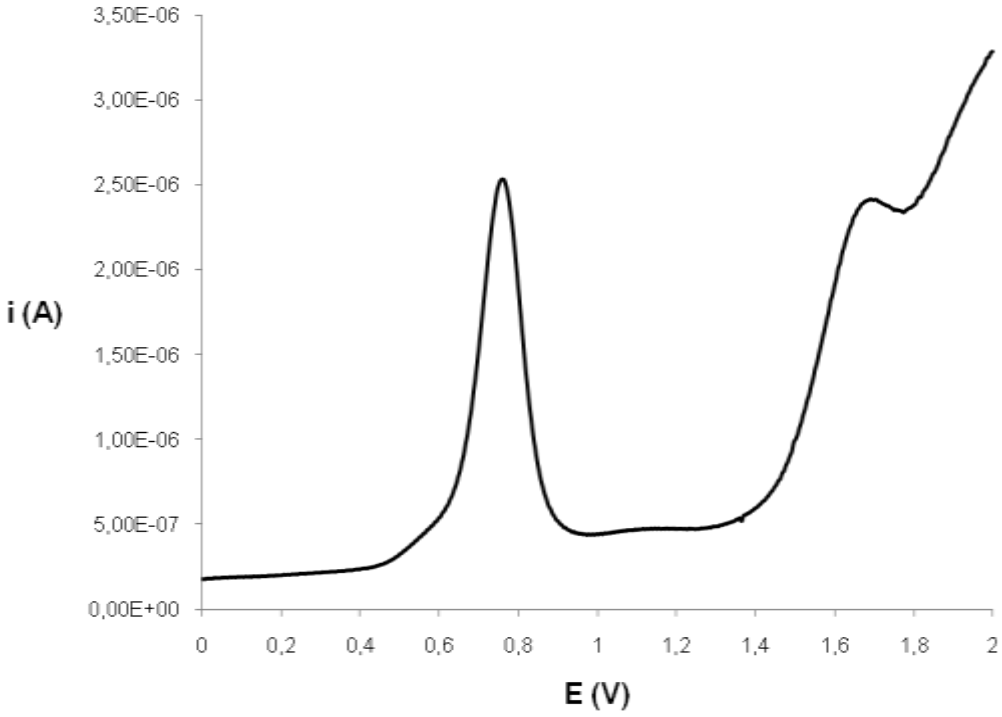

Figure 1. Square-wave voltammogram of complex **5**, 1 mM in CH_2Cl_2 at 20°C ; Frequency : 20 Hz, step potential 5 mV, amplitude 20 mV ; Pt disk working electrode, Pt wire counter electrode, saturated calomel reference electrode ; Supporting electrolyte : nBu$_4$BF$_4$.

Table 1. Crystal data and structure refinement

Identification code	**4**	**5**
Empirical formula	$C_{34}H_{41}ClFeN_2RhS$, CH_2Cl_2, BF_4	$C_{34}H_{40}ClFeN_2RuS$, BF_4
Formula weight	875.69	787.92
Temperature, K	173(2) K	180(2) K
Wavelength, Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic
Space group	P-1	P 2_1/n
a, Å	10.6786(2)	11.8820(3)
b, Å	11.8064(3)	10.2423(2)
c, Å	15.8586(3)	27.5100(7)
α, °	96.8086(18)	90.0
β, °	102.4583(19)	94.493(2)
γ, °	106.009(2).	90.0
Volume, $Å^3$	1842.52(7)	3337.65(14)
Z	2	4
Density (calculated), Mg/m^3	1.578	1.568
Absorption coefficient, mm^{-1}	1.164	1.080
F(000)	892	1608
Crystal size, mm^3	0.38 x 0.30 x 0.10	0.19 x 0.08 x 0.04
Theta range, °	3.06 to 32.95	3.53 to 27.48.
Reflections collected	20287	37401
Independent reflections (R_{int})	12107 (0.0239)	7574 (0.0630)
Completeness, %	98.7	98.6
Absorption correction	Analytical	Multi-scan
Max. and min. transmission	0.896 and 0.720	1.0 and 0.934
Refinement method	F^2	F^2
Data / restraints / parameters	12107 / 413 / 484	7574 / 0 / 412
Goodness-of-fit on F^2	1.074	1.071
R1, wR2 [I>2σ(I)]	0.0331, 0.0810	0.0512, 0.0970
R1, wR2 (all data)	0.0428, 0.0856	0.0811, 0.1073
Residual density, $e.Å^{-3}$	0.656 / -0.503	0.694 / -0.712

Table 2. Selected bond lengths [Å] and angles [°] for complexes **4** and **5**.

Complex	4 (M = Rh)	5 (M = Ru)
M1-Cg1	1.8334(8)	1.7460(15)
M1-Cl1	2.3785(4)	2.3944(9)
M1-S1	2.3622(4)	2.3501(10)
M1-C5	2.0550(17)	2.091(4)
Fe1-Cg2	1.6439(10)	1.645(2)
Fe1-Cg3	1.6485(11)	1.648(2)
S1-C2	1.822(2)	1.798(4)
S1-C18	1.7631(19)	1.774(4)
C2-C3	1.524(3)	1.510(6)
C3-N4	1.459(2)	1.454(6)
N4-C5	1.358(2)	1.369(5)
C5-N6	1.358(2)	1.363(5)
N6-C7	1.391(2)	1.384(5)
N6-C9	1.449(2)	1.445(5)
C7-C8	1.341(3)	1.331(7)
C8-N4	1.384(2)	1.382(5)

	4 (M = Rh)	5 (M = Ru)
Cg1-M1-Cl1	119.92(3)	125.09(6)
Cg1-M1-S1	123.28(3)	119.72(6)
Cg1-M1-C5	133.87(6)	134.56(12)
Cl1-M1-S1	90.407(16)	91.66(4)
Cl1-M1-C5	91.64(5)	81.79(11)
S1-M1-C5	85.68(5)	91.54(12)
Cg2-Fe1-Cg3	179.18(5)	177.42(12)
M1-C5-N4	120.93(12)	125.8(3)
M1-C5-N6	134.66(13)	130.8(3)
N4-C5-N6	104.02(14)	103.0(3)
S1-C2-C3-N4	-50.5(2)	-73.3(4)

Cg1 defines the centroid of the cycle above the metal; Cg2 and Cg3 define the centroid of the cyclopentadienyl groups of ferrocene.