Supporting Information

Singlet Diradical Complexes of Ruthenium and Osmium: Geometrical and Electronic Structures and their Unexpected Changes on Oxidation

Subhas Samanta, Priti Singh, Jan Fiedler, Stanislav Záliš, Wolfgang Kaim, and Sreebrata Goswami**

Table S1. DFT (G03/PBE0) calculated one-electron energies and compositions of selected highest occupied and lowest unoccupied molecular orbitals of $[RuL_2]$ expressed in terms of composing fragments.

MO	E (eV)	Prevailing character	Ru	L
LUMO + 5	-0.05	L + Ru	15	85
LUMO + 4	-0.24	L +Ru	31	69
LUMO + 3	-0.67	L	6	94
LUMO + 2	-0.80	L +Ru	1	99
LUMO + 1	-2.42	L +Ru	15	85
LUMO	-2.45	L +Ru	14	86
HOMO	-4.65	L +Ru	27	73
HOMO-1	-5.07	L	1	99
HOMO-2	-6.01	Ru+ L	56	44
HOMO-3	-6.04	Ru+ L	55	45
HOMO-4	-6.44	Ru+ L	46	54
HOMO-5	-6.60	L	2	98

Table S2. DFT (G03/PBE0) calculated one-electron energies and compositions of selected highest occupied and lowest unoccupied molecular orbitals of $[OsL_2]$ expressed in terms of composing fragments.

MO	E (eV)	Prevailing character	Os	L
LUMO + 5	-0.14	L	6	94
LUMO + 4	-0.27	L	7	93
LUMO + 3	-0.67	L	2	98
LUMO + 2	-0.91	L	2	98
LUMO + 1	-2.35	L + Os	21	79
LUMO	-2.48	L + Os	20	80
HOMO	-4.63	L + Os	25	75
HOMO-1	-5.17	L	3	97
HOMO-2	-6.16	Os + L	46	54
HOMO-3	-6.22	Os + L	52	48
HOMO-4	-6.49	Os + L	37	63
HOMO-5	-6.71	L	1	99

Figure Captions

Figure S1. ESI-MS Spectrum of **3a** in CH_2Cl_2 : (a) observed and (b) simulated.

Figure S2. ^{1}H NMR Spectrum of **2a** in d^6-DMSO.

Figure S3. Cyclic voltammograms of the complexes **2a** and **3a** $[M(L^a)_2]$ in CH_2Cl_2/0.1 M Bu_4NClO_4.

Figure S1

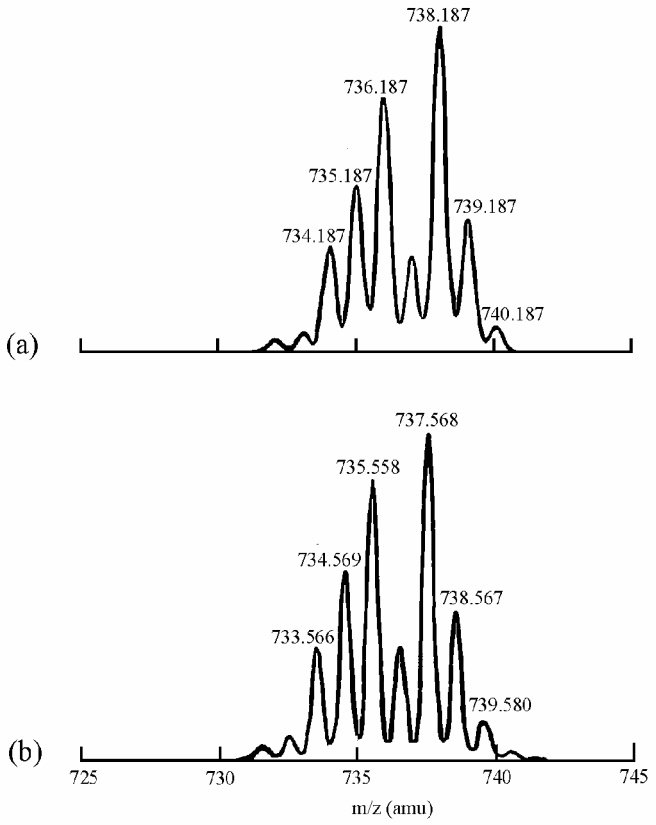
738.187
736.187
735.187
739.187
734.187
740.187
(a)
737.568
735.558
734.569
738.567
733.566
739.580
(b)
725
730
735
740
745
m/z (amu)

Figure S2

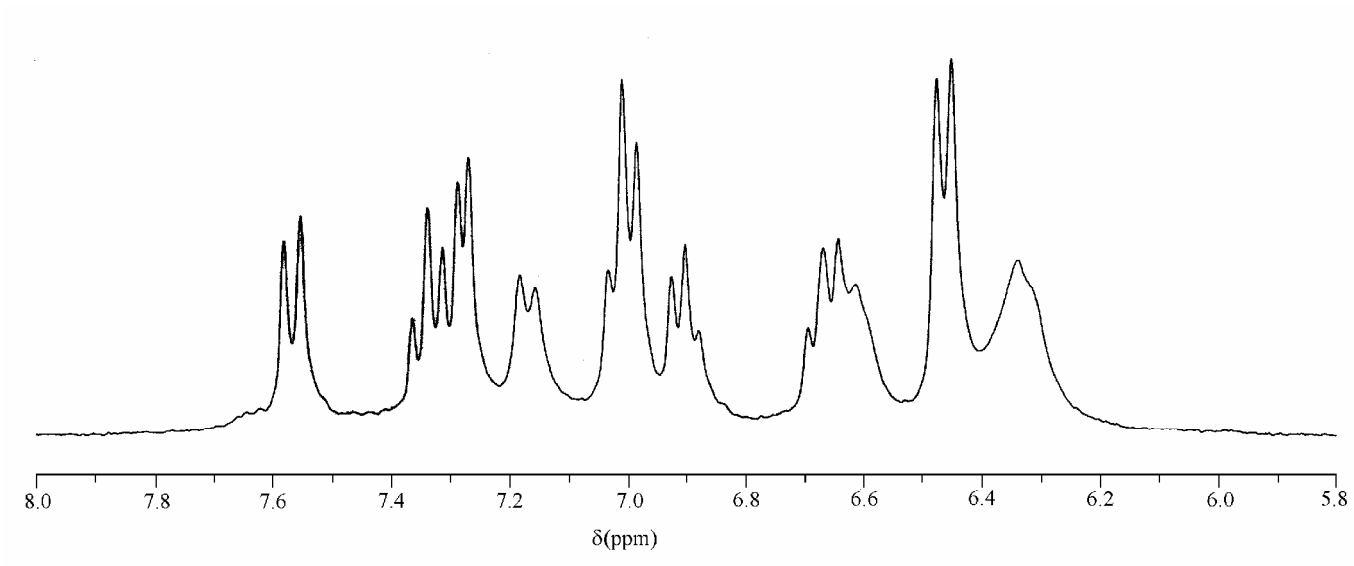
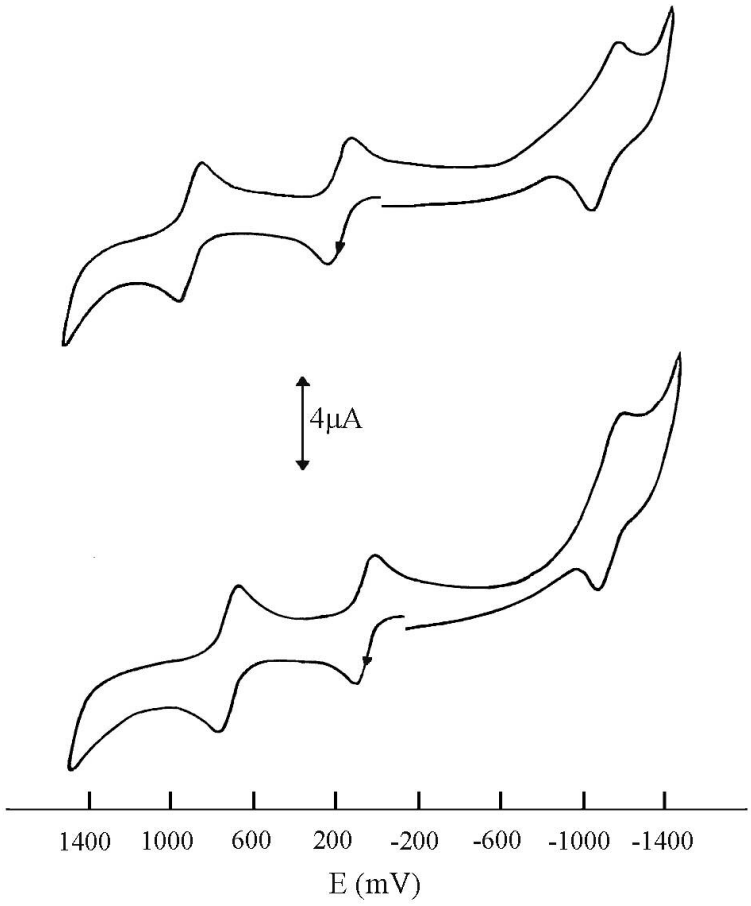
Figure S3