*Supplementary Materials*

*for*

# Half-Sandwich Ru(II) and Os(II) Bathophenanthroline Complexes Containing a Releasable Dichloroacetato Ligand

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***Synthesis***

The formerly reported protocol for the preparation of complex **Ru-Cl** [1] was modified, as described below, and this modification was used also for the Os(II) analogue **Os-Cl**. The starting dimer [M(μ-Cl)(η$^6$-*p*cym)Cl]$_2$ (0.10 mmol; M = Ru or Os) reacted with an excess (0.15 mmol) of bphen in 5 mL of MeOH in a microwave reaction system (100 °C, 1 min). The obtained solutions were cooled to ambient temperature, and an excess of $NH_4PF_6$ (3.0 mmol) was added. The solvent volume was reduced after 15 min of stirring at ambient temperature, until the solid formed. The obtained chlorido complexes [Ru(η$^6$-*p*cym)(bphen)Cl]$PF_6$ (**Ru-Cl**) and [Os(η$^6$-*p*cym)(bphen)Cl]$PF_6$ (**Os-Cl**) were collected by filtration, washed (1 × 0.5 mL of MeOH and 3 × 1 mL of diethyl ether) and dried under vacuum.

*Anal.* Calcd. for $C_{34}H_{30}N_2ClRuPF_6$ (**Ru-Cl**): C, 54.59; H, 4.04; N, 3.74%; found: C, 54.46; H, 3.92; N, 3.59%. $^1$H NMR (DMSO-$d_6$, ppm): $\delta$ 10.01 (d, $J$ = 5.5 Hz, C2–H, 2H), 8.16 (d, $J$ = 5.5 Hz, C3–H, 2H), 8.13 (s, C5–H, 2H), 7.65 (m, C9–H, C10–H, C11–H, 10H), 6.40 (d, $J$ = 6.4 Hz, C23–H, 2H), 6.20 (d, $J$ = 6.4 Hz, C22–H, 2H), 2.72 (sep, $J$ = 6.4 Hz, C25–H, 1H), 2.19 (s, C27–H, 3H), 1.02 (d, $J$ = 6.4 Hz, C26–H, 6H). $^{13}$C NMR (DMSO-$d_6$, ppm): $\delta$ 155.8 (C2), 150.0 (C4), 145.9 (C7), 134.9 (C12), 130.0–127.6 (C6, C9, C10, C11), 125.5 (C5), 104.8 (C21), 102.2 (C24), 85.9 (C23), 84.5 (C22), 30.5 (C25), 21.8 (C26), 18.2 (C27). ESI+ MS (methanol, $m/z$): 603.1 (calc. 603.1; 100%; [Ru(*p*cym)(bphen)Cl]$^+$). IR (ATR, cm$^{-1}$): 408, 461, 490, 515, 556, 636, 670, 699, 736, 764, 836, 925, 999, 1030, 1079, 1160, 1229, 1298, 1403, 1444, 1469, 1494, 1517, 1559, 1598, 1621, 2872, 2932, 2968, 3030, 3050, 3090.

*Anal.* Calcd. for $C_{34}H_{30}N_2ClOsPF_6$ (**Os-Cl**): C, 48.77; H, 3.61; N, 3.35%; found: C, 48.80; H, 3.46; N, 3.27%. $^1$H NMR (DMSO-$d_6$, ppm): $\delta$ 9.95 (d, $J$ = 5.5 Hz, C2–H, 2H), 8.19 (s, C5–H, 2H), 8.13 (d, $J$ = 5.5 Hz, C3–H, 2H), 7.70 (m, C9–H, C10–H, C11–H, 10H), 6.62 (d, $J$ = 5.9 Hz, C23–H, 2H), 6.37 (d, $J$ = 5.9 Hz, C22–H, 2H), 2.57 (m, C25–H, 1H), 2.25 (s, C27–H, 3H), 0.95 (d, $J$ = 6.4 Hz, C26–H, 6H). $^{13}$C NMR (DMSO-$d_6$, ppm): $\delta$ 155.6 (C2), 150.1 (C4), 147.0 (C7), 134.8 (C12), 130.2–127.8 (C6, C9, C10, C11), 125.9 (C5), 95.5 (C21), 94.9 (C24), 77.5 (C23), 75.0 (C22), 30.6 (C25), 22.1 (C26), 18.1 (C27). ESI+ MS (methanol, $m/z$): 693.2 (calc. 693.2; 100%; [Os(*p*cym)(bphen)Cl]$^+$). IR (ATR, cm$^{-1}$): 407, 465, 489, 555, 637, 669, 699, 734, 764, 833, 927, 999, 1029, 1055, 1079, 1154, 1185, 1230, 1273, 1300, 1404, 1444, 1468, 1493, 1516, 1557, 1600, 1624, 2876, 2933, 2967, 3029, 3052, 3092.

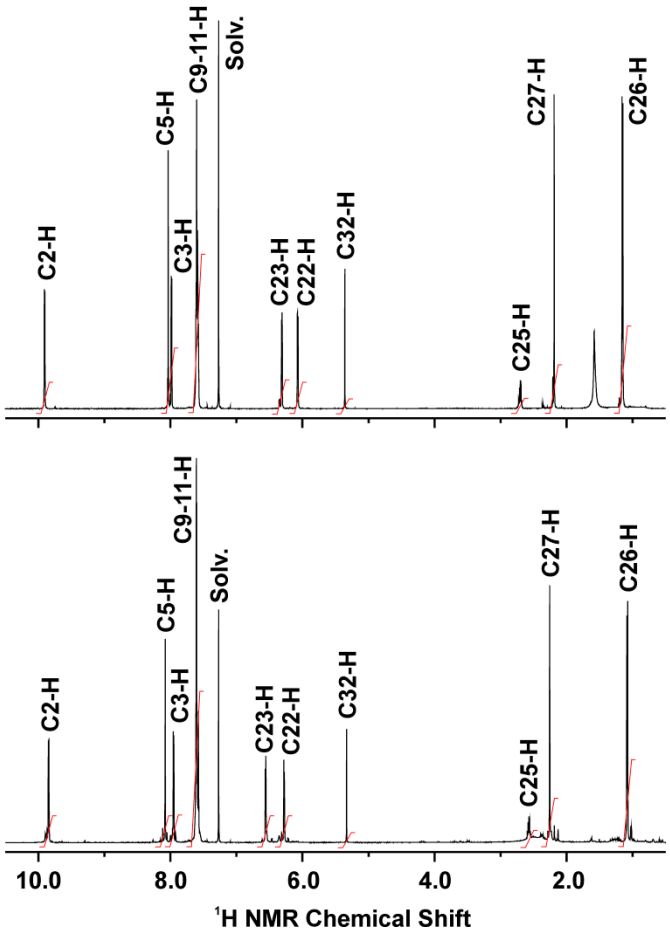


**Figure S1.** $^{1}$H NMR spectra ($CDCl_3$ solutions) of complexes **Ru-dca** (*bottom*) and **Os-dca** (*top*) given together with the assignment of the detected signals.

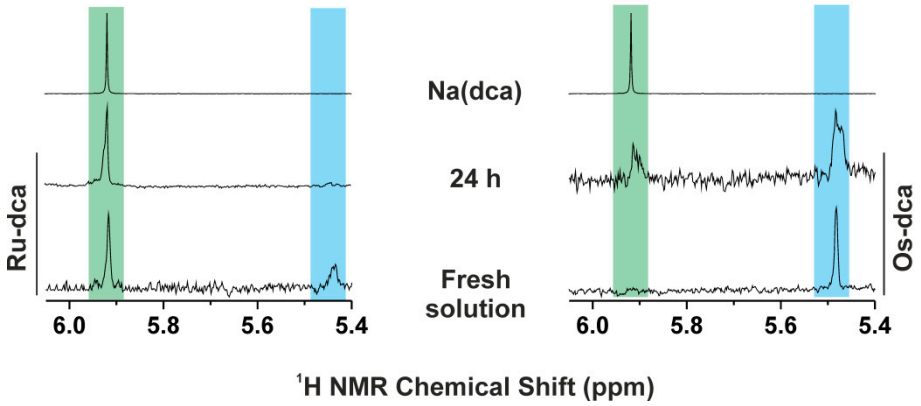


**Figure S2.** The selected results of the time-dependent $^{1}$H NMR studies of the progress of the dca ligand release of complexes **Ru-dca** and **Os-dca** dissolved in 20% MeOD-$d_4$/80% $D_2O$. The signals of the C32–H hydrogen atom of the coordinated and released dca is depicted in blue, and green, respectively.

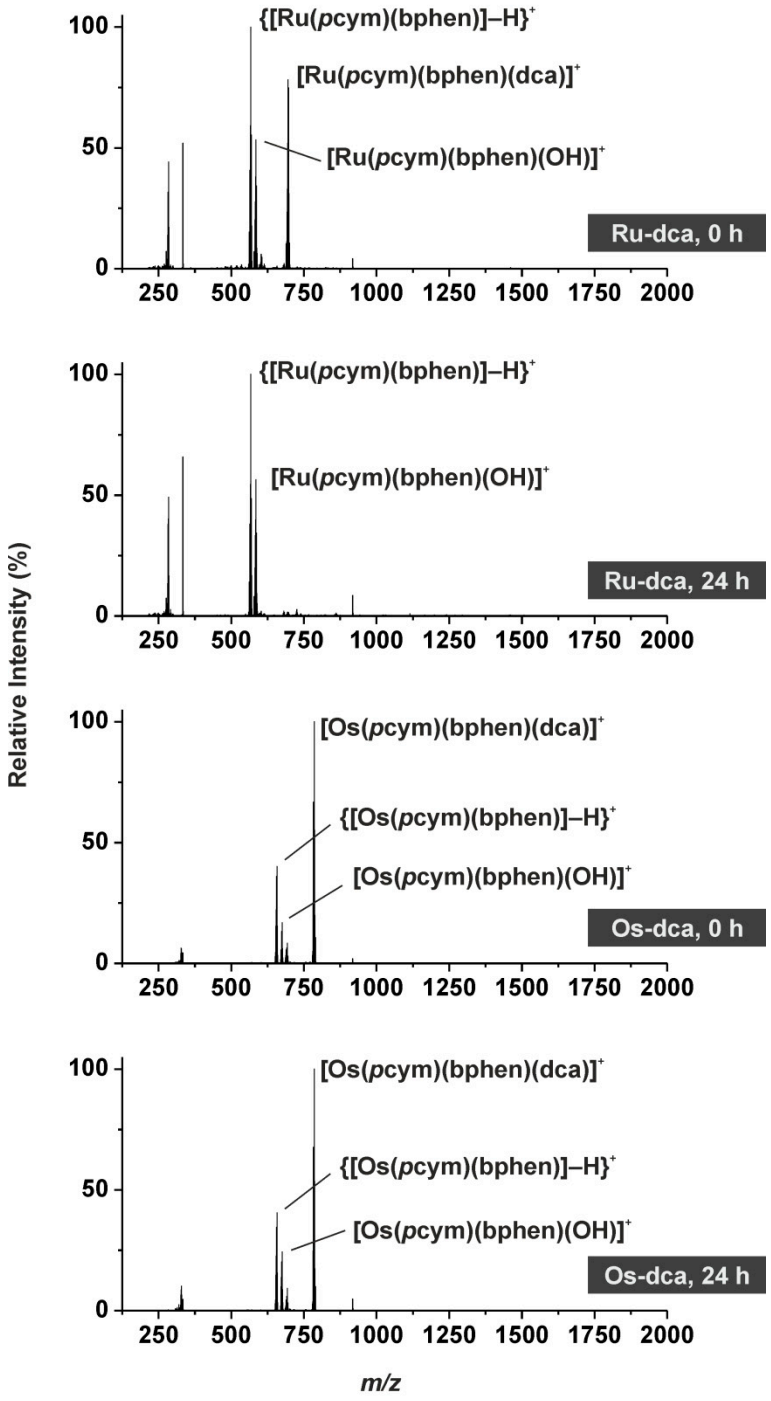


**Figure S3.** ESI+ mass spectra of complexes **Ru-dca** and **Os-dca** dissolved in methanol/water (1:1, *v/v*) obtained at various time points.

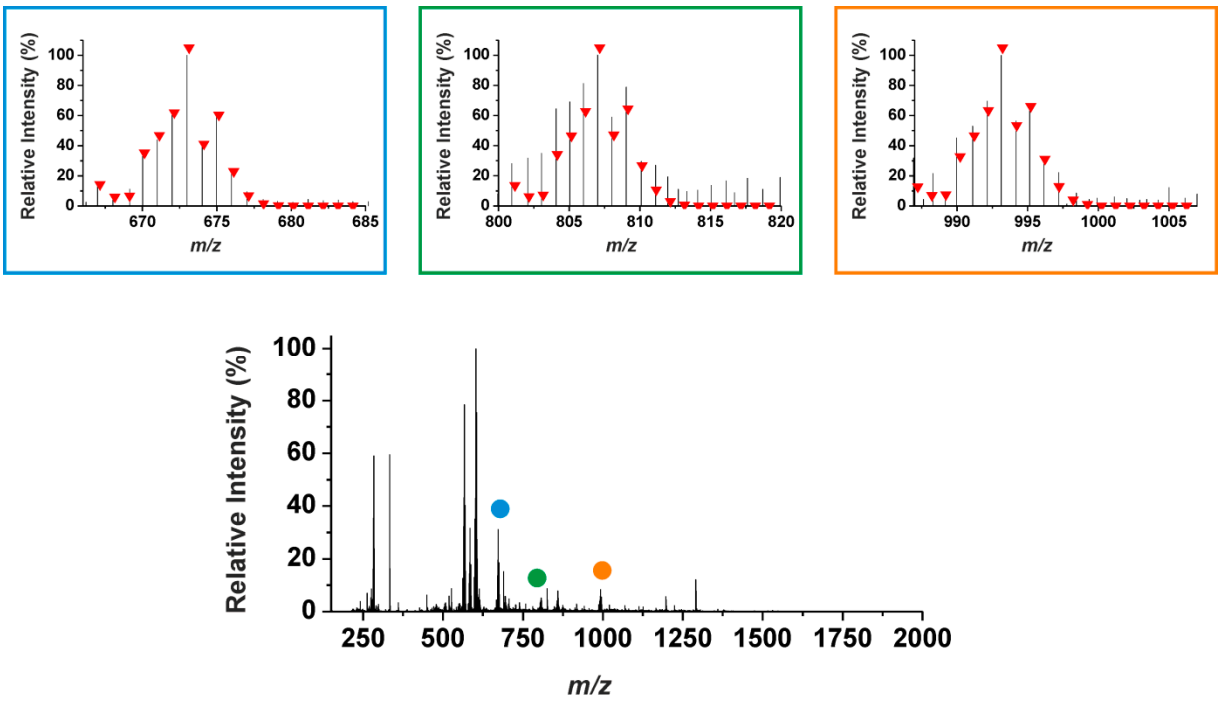


**Figure S4.** ESI+ mass spectra of the mixture of complex **Ru-dca** and GSH (6 μM final concentration) and CySH (290 μM final concentration) in methanol/water (1:1, *v/v*) recorded after 24 h of standing at ambient temperature. The peaks of the adducts of {[Ru(*p*cym)(bphen)]–H}$^{+}$ with either two CyS (or one cystine (CySSCy); 807.2 *m/z*; green sphere) or with CyS and GS (or their disulfide CySSG; 993.2 *m/z*; orange sphere) and the adduct of {[Ru(*p*cym)(bphen)]+($HL^3$)–H}$^{+}$ with deaminated cysteine (*i.e.*, 3-sulfanylpropanoic acid; $HL^3$; 673.0 *m/z*; blue sphere) are given in detail together with the calculated isotopic distribution (red triangles).

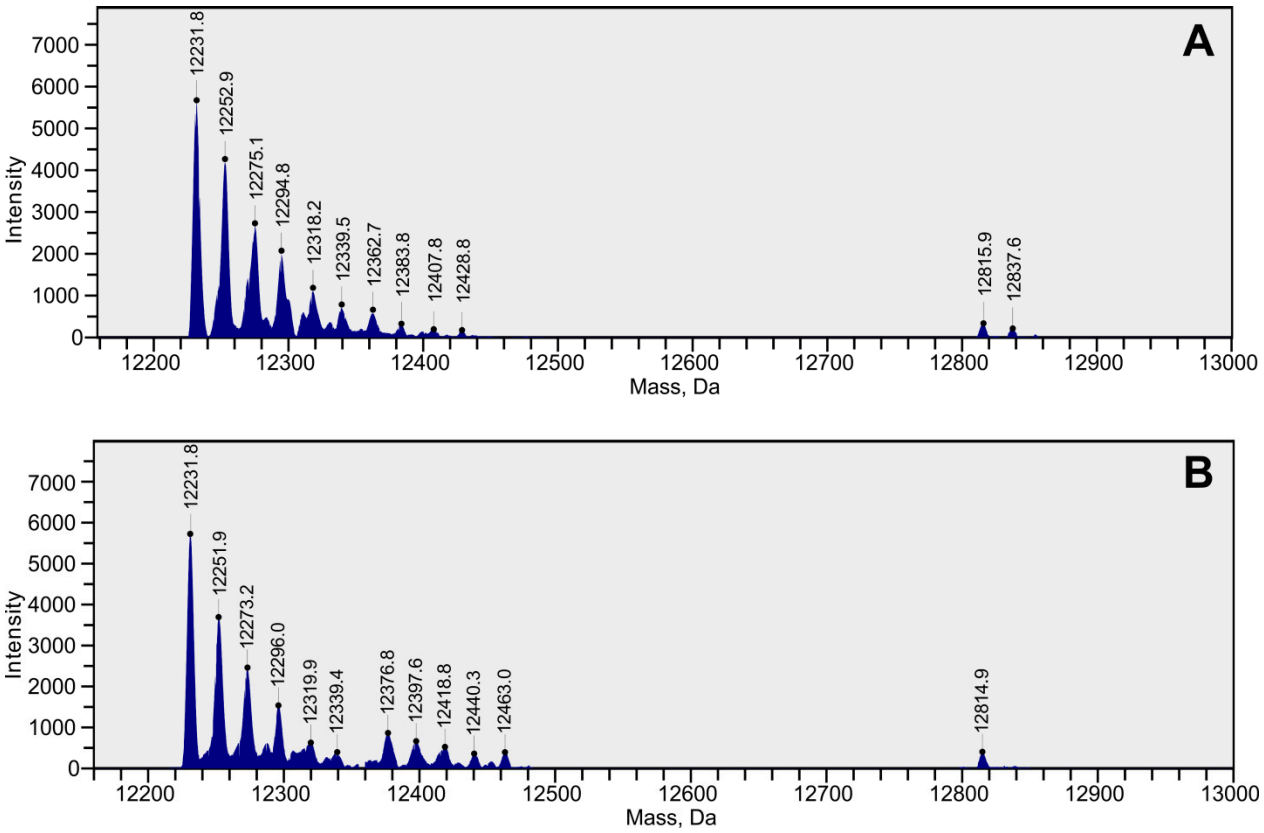


**Figure S5.** Deconvoluted neutral mass spectra of cytochrome c (Cytc; A) and its mixture (3 μM final concentration) with complex **Ru-dca** (10 μM final concentration) (B), both dissolved in MeOH/$H_2O$ (1:1, *v/v*). The mass spectra were recorded after 24 h of standing at room temperature and show the formation of a minor adduct of Cytc with $PF_6^-$, characterized by the mass difference of 145 Da (difference between the main peak of Cytc at 12231.8 Da and main peak of the {Cytc–$PF_6$} adduct at 12376.8 Da).

## References

[1] Betanzos-Lara, S.; Novakova, O.; Deeth, R.J.; Pizarro, A.M.; Clarkson, G.J. Liskova, B.; Brabec, V.; Sadler, P.J.; Habtemariam, A. Bipyrimidine ruthenium(II) arene complexes: structure, reactivity and cytotoxicity. *J. Biol. Inorg. Chem.* **2012**, *17*, 1033–1051.