Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

The stepwise generation of multimetallic complexes based on a vinylbipyridine linkage and their photophysical properties

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The X-ray structure of [Ru{CH=CH-bpyReCl(CO)$_3$}Cl(CO)(BTD)(PPh$_3$)$_2$] (3)

Crystal data for **3**: $C_{58}H_{43}Cl_2N_4O_4P_2ReRuS \cdot 2(CH_2Cl_2)$, M = 1481.98, triclinic, P-1 (no. 2), a = 13.4717(5), b = 15.1437(5), c = 18.2941(5) Å, α = 66.909(3), β = 74.098(3), γ = 64.648(4)°, V = 3077.2(2) Å^3, Z = 2, D_c = 1.599 g cm^{-3}, μ(Mo-Kα) = 2.605 mm^{-1}, T = 173 K, orange blocks, Agilent Xcalibur 3 E diffractometer; 12133 independent measured reflections (R_{int} = 0.0202), F^2 refinement,[S1] R_1(obs) = 0.0345, wR_2(all) = 0.0790, 10044 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{full}$ = 50°], 671 parameters. CCDC 1504933.

The chloride ligand bound to the rhenium centre and the associated *trans* carbonyl group were found to be disordered above and below the bipyridyl plane. The two orientations were found to be of *ca*. 86 (chloride 'above' and carbonyl 'below') and 14% occupancy (carbonyl 'above' and chloride 'below'), their geometries were optimised, the thermal parameters of equivalent atoms were restrained to be similar, and only the atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically).

The included solvent was found to be highly disordered, and the best approach to handling this diffuse electron density was found to be the SQUEEZE routine of PLATON.[S2] This suggested a total of 167 electrons per unit cell, equivalent to 83.5 electrons per complex. Before the use of SQUEEZE the solvent clearly resembled dichloromethane (CH_2Cl_2, 42 electrons), and 2 dichloromethane molecules corresponds to 84 electrons, so this was used as the solvent present. As a result, the atom list for the asymmetric unit is low by 2(CH_2Cl_2) =

$C_2H_4Cl_4$ (and that for the unit cell low by $C_4H_8Cl_8$) compared to what is actually presumed to be present.

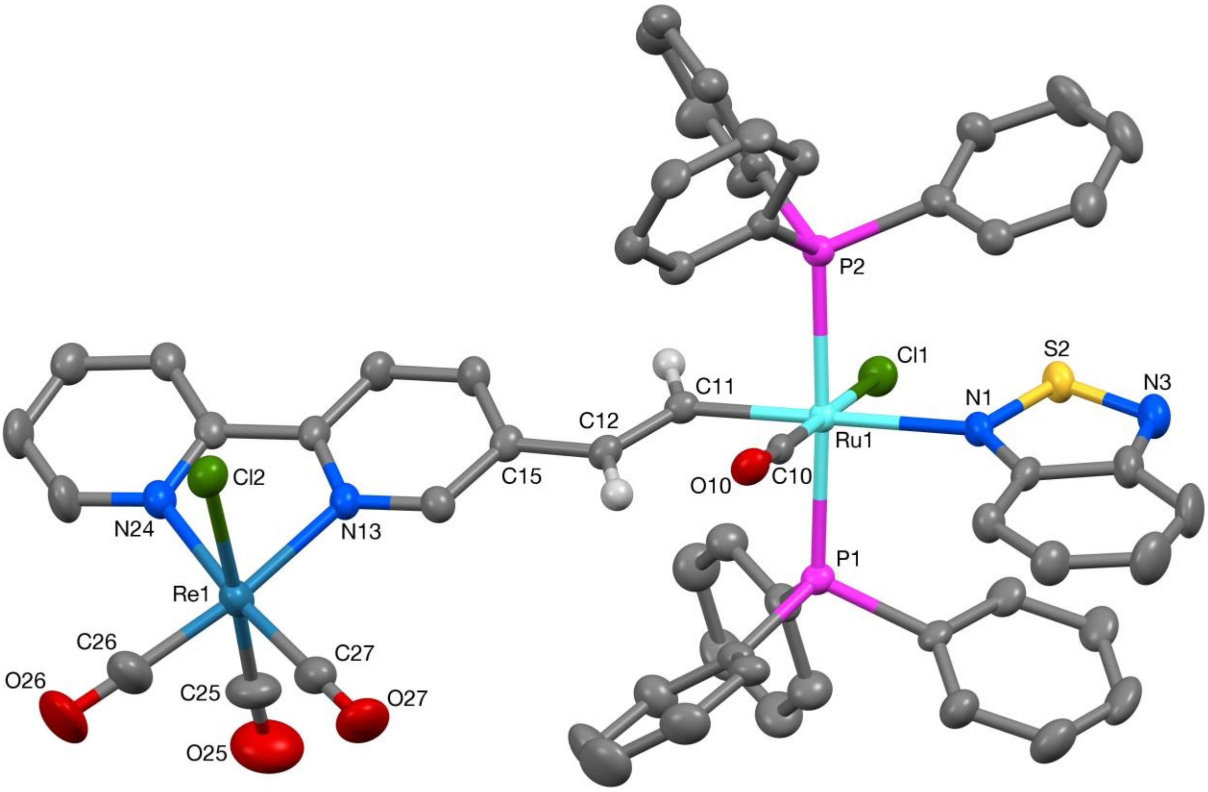

Figure S1. The structure of **3** (50% probability ellipsoids).

The X-ray structure of [Os{CH=CHbpyReCl(CO)$_3$}{S$_2$P(OEt)$_2$}(CO)(PPh$_3$)$_2$] (6)

Crystal data for **6**: $C_{56}H_{49}ClN_2O_6OsP_3ReS_2$, M = 1414.85, triclinic, P-1 (no. 2), a = 11.9380(4), b = 17.1986(5), c = 17.6149(7) Å, α = 86.006(3), β = 89.093(3), γ = 70.522(3)°, V = 3401.3(2) Å^3, Z = 2, D_c = 1.381 g cm^{-3}, μ(Cu-Kα) = 8.835 mm^{-1}, T = 173 K, orange needles, Agilent Xcalibur PX Ultra A diffractometer; 9468 independent measured reflections (R_{int} = 0.0296), F^2 refinement,[S1] R_1(obs) = 0.0809, wR_2(all) = 0.2493, 7949 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 147°], 662 parameters. CCDC 1406199.

The crystals of [Os{CH=CH-bpyReCl(CO)$_3$}{S$_2$P(OEt)$_2$}(CO)(PPh$_3$)$_2$] (**6**) were severely twinned. A number of different crystals were tried, three of which led to data collections. Unfortunately, despite efforts to remove the twinning by cutting the crystals, all three of these data sets still show significant twinning, and attempts to fully address this in the data processing were unsuccessful. An additional issue, which was not understood until much later, caused the initial data set to be incomplete. The array of lattice points associated with the triclinic unit cell (that is evidently the correct unit cell) can be fairly well matched to a *C*-face centred monoclinic unit cell. The first data collection assumed the higher symmetry cell, and so ended up short of data. The second attempt took this into consideration and the initial cell was transformed into the triclinic counterpart. Unfortunately, the data collection software still collected data based on the *C*-face centred monoclinic unit cell, and likewise for the third data set. Though it was noticed that the data sets were incomplete, the reason was not discovered for a number of months, by which time the original sample had desolvated and so no new data could be collected. The best of these data sets (the second) is thus only *ca*. 73% complete. When new crystals were subsequently obtained many months later, they again proved to be severely twinned. For the best of these a complete data set was collected, but the best structural model that could be produced was significantly poorer than the one reported here.

An additional problem apparent in the refinements concerns a large residual electron density peak near the rhenium centre. The top peak stands out from the rest at *ca*. 8.8 $eÅ^{-3}$ with the next four peaks being *ca*. 1.5, 1.4, 1.3 and 1.3 $eÅ^{-3}$. This large peak is situated *ca*. 0.9 Å away from the rhenium atom and *ca*. 1.1 Å from the carbon of the O(64) carbonyl group, and lies approximately along the Re1–CO(64) vector, the Q1···Re–C angle being *ca*. 26°. There is no sensible chemical explanation for such a large peak at this position, so it is almost certainly an artefact of the twinning.

The chloride ligand bound to the rhenium centre and the associated *trans* carbonyl group were found to be disordered above and below the bipyridyl plane. The two orientations were found to be of *ca*. 64 (chloride “above” and carbonyl “below”) and 36% occupancy (carbonyl “above” and chloride “below”), their geometries were optimised, the thermal parameters of equivalent atoms were restrained to be similar, and only the atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically).

Despite all the obvious problems with the structure, there is still some useful information that can be gleaned from it. The basic identity of the compound and its connectivity are pretty clear (though the assignment of the rhenium and osmium centres was based on other information). So, while the structure, shown in Figure S1, is not ideal, it does provide additional information to the spectroscopic data.

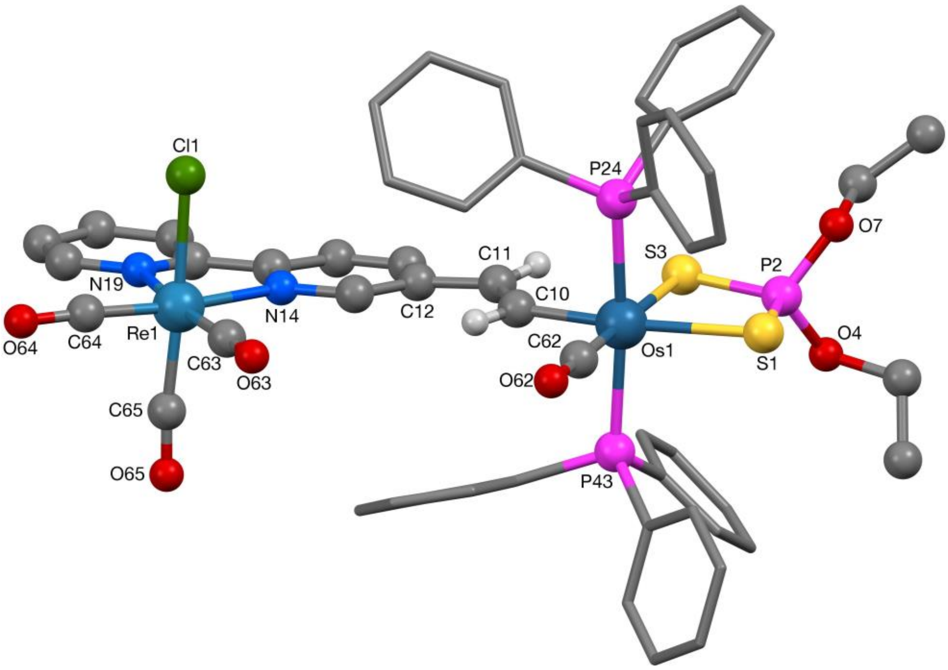

Figure S2. The structure of $[Os\{CH{=}CH\text{-}bpyReCl(CO)_3\}\{S_2P(OEt)_2\}(CO)(PPh_3)_2]$ (**6**) with 50% probability ellipsoids.

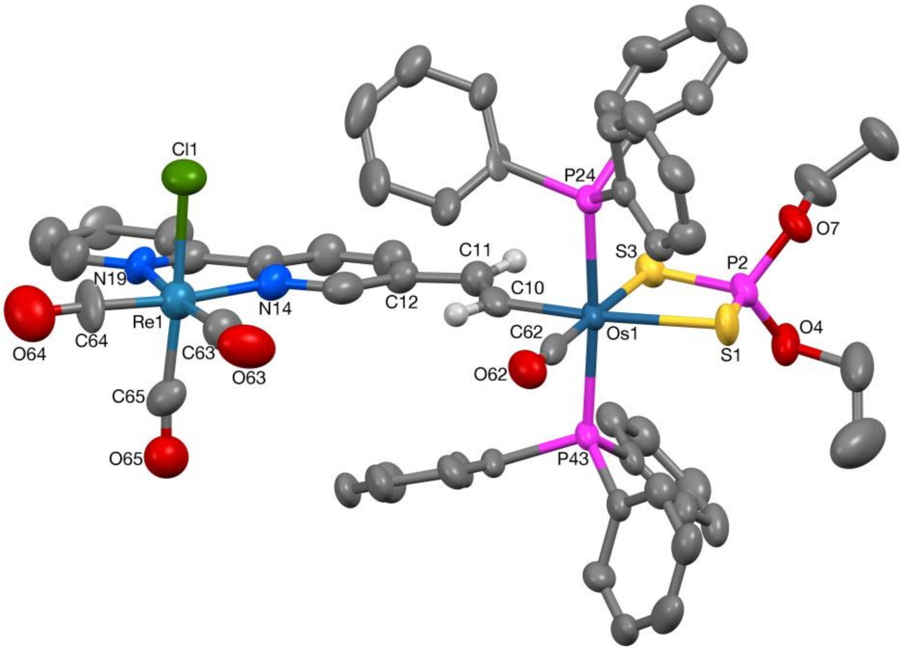

Figure S3. The structure of **6** (50% probability ellipsoids).

UV-vis absorption spectroscopy

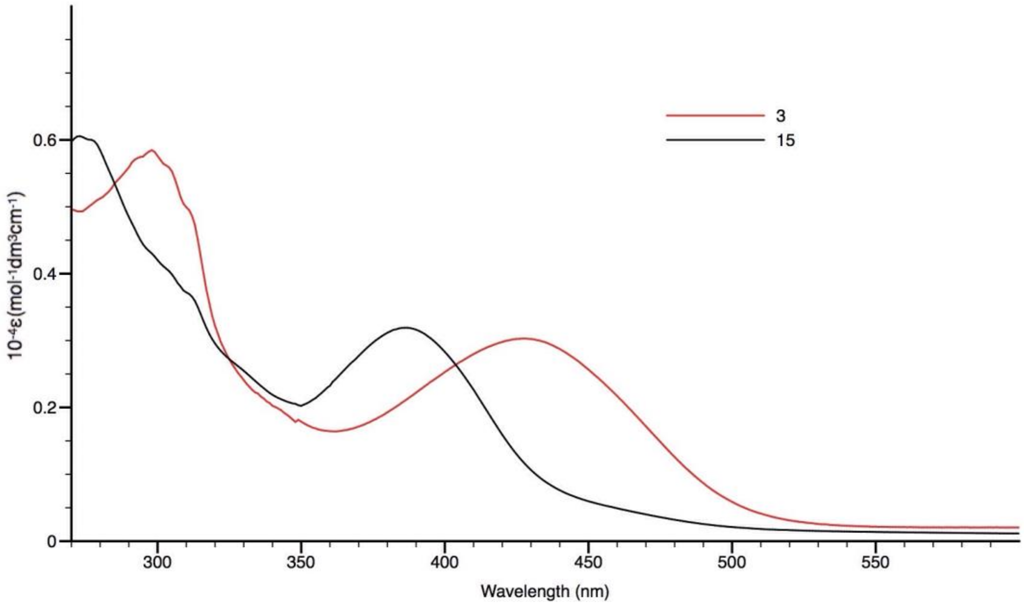

Figure S4. Absorption profiles of complexes [Ru{CH=CH-bpyReCl$(CO)_3$}Cl(CO)(BTD)$(PPh_3)_2$] (**3**) (red trace) and [Ru{CH=CH-bpyReCl$(CO)_3$}Cl$(CO)_2$$(PPh_3)_2$] (**15**) (black trace) in 10^{-5} M CH_2Cl_2 solution, 298 K.

Emission spectroscopy

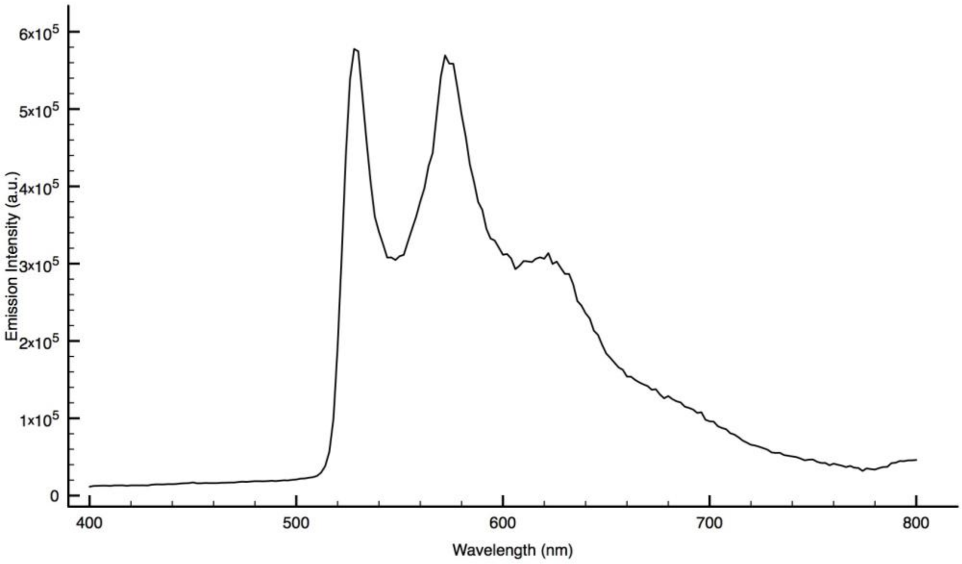

Figure S5. Emission profile of complex [Ru{CH=CH-bpyReCl$(CO)_3$}Cl(CO)(BTD)$(PPh_3)_2$] (**3**) in CH_2Cl_2 frozen at 77K. λexc = 400 nm.

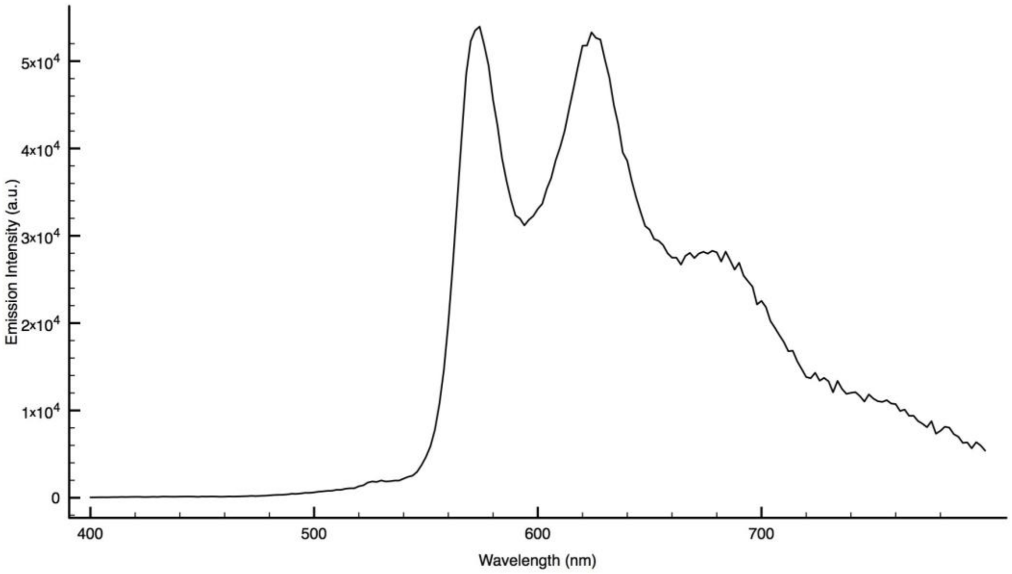

Figure S6. Emission profile of complex [Ru{CH=CH-bpyReCl$(CO)_3$}Cl$(CO)_2$$(PPh_3)_2$] (**15**) in CH_2Cl_2 frozen at 77K. λexc = 400 nm.

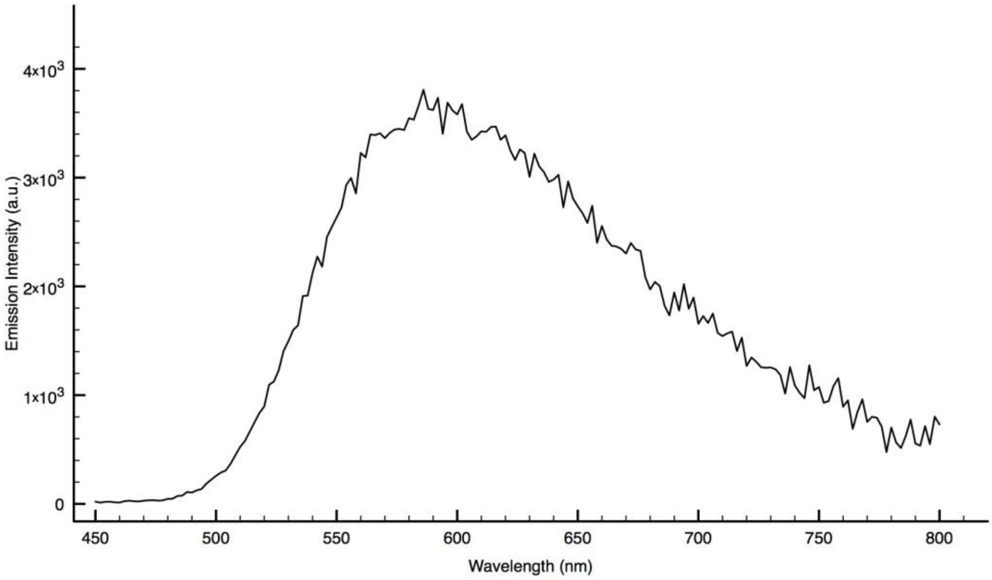

Figure S7. Emission profile of complex [Os{CH=CH-bpyReCl$(CO)_3$}Cl(CO)(BTD)$(PPh_3)_2$] (**4**) in air-equilibrated CH_2Cl_2 at 298 K. λ_{exc} = 400 nm.

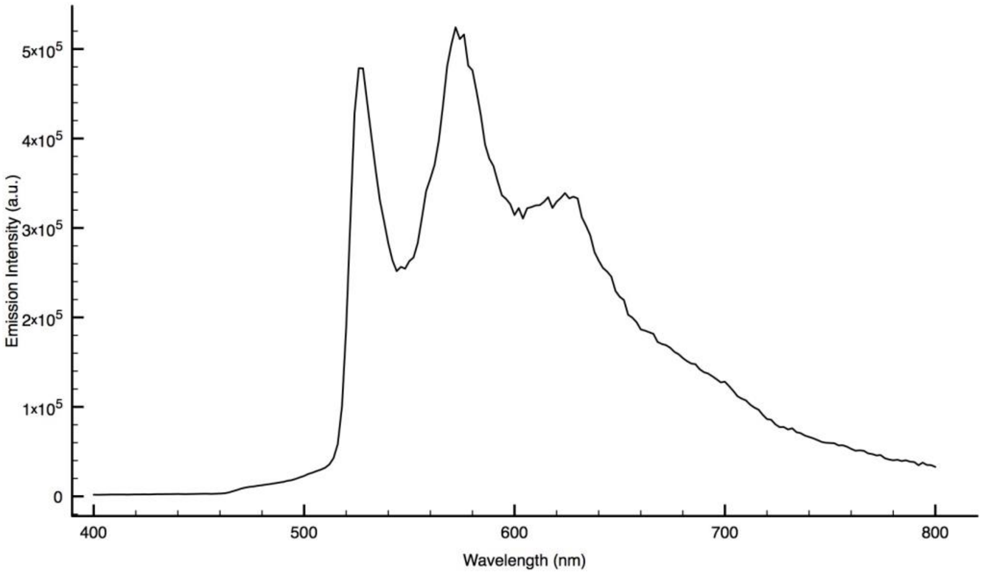

Figure S8. Emission profile of [Os{CH=CH-bpyReCl$(CO)_3$}Cl(CO)(BTD)$(PPh_3)_2$] (**4**) in CH_2Cl_2 frozen at 77K. λexc = 400 nm.

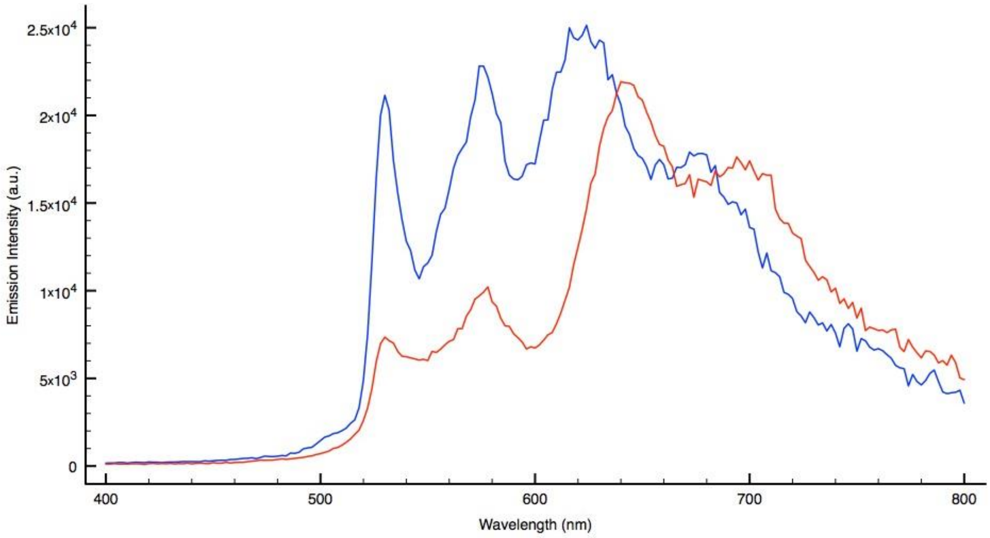

Figure S9. Emission profiles of [Ru{CH=CH-bpyReCl$(CO)_3$}{$S_2P(OEt)_2$}(CO)$(PPh_3)_2$], (5) (blue trace) and [Os{CH=CH-bpyReCl$(CO)_3$}{$S_2P(OEt)_2$}(CO)$(PPh_3)_2$] (**6**) (red trace) in CH_2Cl_2 frozen at 77K. λexc = 400 nm

References

S1 (a) SHELXTL, Bruker AXS, Madison, WI; (b) SHELX-97, G. M. Sheldrick, *Acta Cryst*., 2008, **A64**, 112-122; (c) SHELX-2013, G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.

S2 A. L. Spek (2003, 2009) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands. See also A. L. Spek, *Acta. Cryst.*, 2015, **C71**, 9-18.