Supporting Information

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

Anita Toscani, Khairil Anuar Jantan, Jubeda B. Hena, Jonathan A. Robson, Emily J. Parmenter, Valentina Fiorini, Andrew J. P. White, Stefano Stagni and James D. E. T. Wilton-Ely*

The X-ray structure of [Ru{CH=CH-bpyReCl(CO)₃}Cl(CO)(BTD)(PPh₃)₂] (3)

Crystal data for 3: C₅₈H₄₅Cl₂N₄O₄P₂ReRuS·2(CH₂Cl₂), 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) Å³, Z = 2, Dₐ = 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), F² refinement, S1 R₁(obs) = 0.0345, wR₂(all) = 0.0790, 10044 independent observed absorption-corrected reflections [|Fₒ| > 4σ(|Fₒ|), 2θ 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. 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 (CH₂Cl₂, 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(CH₂Cl₂) =
C$_2$H$_4$Cl$_4$ (and that for the unit cell low by C$_4$H$_8$Cl$_8$) 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=CH$_2$-bpyReCl(CO)$_3$}${S_2P(OEt)$_2$}(CO)(PPh$_3$)$_2$] (6)**

Crystal data for 6: C$_{56}$H$_{49}$ClN$_2$O$_6$OsP$_3$Re$_2$, $M = 1414.85$, triclinic, $P$-1 (no. 2), $a = 11.9380(4)$, $b = 17.1986(5)$, $c = 17.6149(7)$ Å, $\alpha = 86.006(3)$, $\beta = 89.093(3)$, $\gamma = 70.522(3)$°, $V = 3401.3(2)$ Å$^3$, $Z = 2$, $D_c = 1.381$ g cm$^{-3}$, $\mu$(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, $^1$ $R_1$(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)$_3$}${S_2P(OEt)$_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 \([\text{Os}\{\text{CH}=\text{CH-bpyReCl(CO)}_3\}\{\text{S}_2\text{P(OEt)}_2\}(\text{CO})(\text{PPh}_3)_2]\) \((6)\) 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_{2}Cl_{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_{2}Cl_{2} frozen at 77K. \lambda_{exc} = 400 \text{ nm}.
Figure S6. Emission profile of complex [Ru(CH=CH-bpyReCl(CO)₃)Cl(CO)₂(PPh₃)₂] (15) in CH₂Cl₂ frozen at 77K. λ_{exc} = 400 nm.

Figure S7. Emission profile of complex [Os(CH=CH-bpyReCl(CO)₃)Cl(CO)(BTD)(PPh₃)₂] (4) in air-equilibrated CH₂Cl₂ at 298 K. λ_{exc} = 400 nm.
Figure S8. Emission profile of $[\text{Os}\{\text{CH}=\text{CH}-\text{bpyReCl(CO)}_3\}\text{Cl(CO)(BTD)(PPh}_3\}_2]$ (4) in CH$_2$Cl$_2$ frozen at 77K. $\lambda_{\text{exc}} = 400$ nm.

Figure S9. Emission profiles of $[\text{Ru}\{\text{CH}=\text{CH}-\text{bpyReCl(CO)}_3\}\{\text{S}_2\text{P(OEt)}_2\}(\text{CO})(\text{PPh}_3)_2]$ (5) (blue trace) and $[\text{Os}\{\text{CH}=\text{CH}-\text{bpyReCl(CO)}_3\}\{\text{S}_2\text{P(OEt)}_2\}(\text{CO})(\text{PPh}_3)_2]$ (6) (red trace) in CH$_2$Cl$_2$ frozen at 77K. $\lambda_{\text{exc}} = 400$ 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.