

Supporting Information — X-Ray Crystallography

Manuscript: Dithiocarboxylate complexes of ruthenium(II) and osmium(II) based on *N*-heterocyclic carbenes

Authors: Saira Naeem, Amber L. Thompson, Andrew J.P. White, Lionel Delaude and James D.E.T. Wilton-Ely

The X-ray crystal structure of **4**

The 2,5-diisopropylimidazole unit of the cationic complex, the PF₆ anion, and both of the included dichloromethane solvent sites in the structure of **4** were found to be disordered. For the 2,5-diisopropylimidazole unit, two complete orientations were identified of *ca.* 77 and 23 % occupancy (see Fig. S2). The geometries of the two orientations were restrained to be the same, the thermal parameters of adjacent atoms of the two orientations were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (the rest were refined isotropically). Three orientations were identified for the PF₆ anion, of *ca.* 64, 19 and 17% occupancy, their geometries optimised, the thermal parameters of adjacent atoms of the three orientations restrained to be similar, and only the atoms of the major occupancy orientation were refined anisotropically (the rest were refined isotropically). The included dichloromethane solvent was found to be distributed across two sites, both of which were discovered to be disordered. For the C(70)-based molecule, two orientations of *ca.* 83 and 17% occupancy were identified, their geometries optimised, the thermal parameters of adjacent atoms of the two orientations restrained to be similar, and only the atoms of the major occupancy orientation were refined anisotropically (the rest were refined isotropically). For the C(80)-based molecule, three orientations of *ca.* 53, 14 and 8% occupancy were identified, their geometries optimised, the thermal parameters of adjacent atoms of the three orientations restrained to be similar, and only the atoms of the major occupancy orientation were refined anisotropically (the rest were refined isotropically); inspection of the thermal parameters suggested that this site was only *ca.* 75% occupied in total.

The X-ray crystal structure of **8**

The crystals of **8** were very small and weak and suffered from solvent loss. Data were collected, however, that solved well although due to the paucity of data, vibrational and thermal similarity restraints were required to maintain sensible atomic displacement

parameters. In addition to the main residue, two molecules of diethyl ether were found in the difference Fourier map. The enlarged ADPs for one of these suggested the possibility of partial occupancy, however, refinement of the occupancy and careful examination of the difference Fourier suggested that this was not the case.

Figures

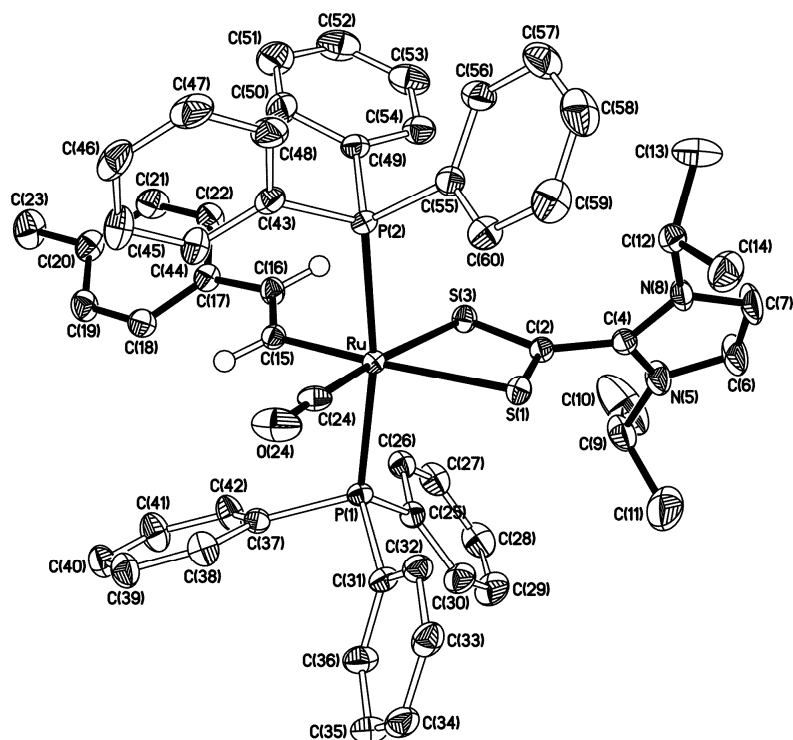


Fig. S1 The molecular structure of the cation present in the structure of **4** (50% probability ellipsoids).

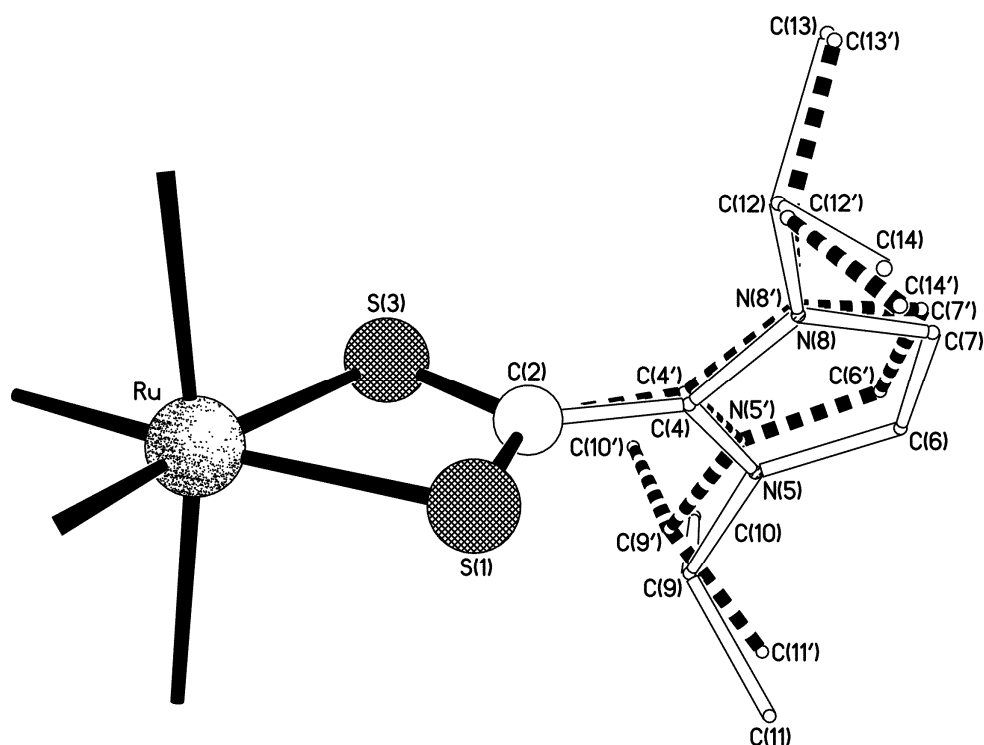


Fig. S2 The disorder of the 2,5-diisopropylimidazole unit in the structure of **4**. The major occupancy orientation (*ca.* 77%) is drawn with open bonds, whilst the minor occupancy orientation (*ca.* 23%) is drawn with dashed bonds.

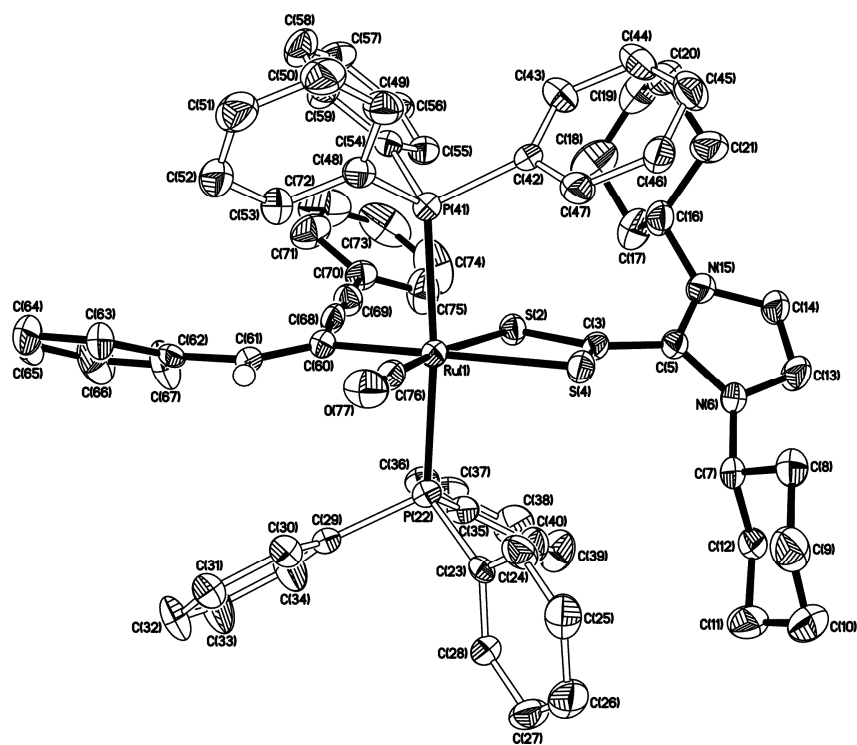


Fig. S3 The molecular structure of the cation present in the structure of **8** (50% probability ellipsoids).