Supporting Information — X-Ray Crystallography

The functionalisation of ruthenium(II) and osmium(II) alkenyl complexes with amine- and alkoxy-terminated dithiocarbamates.

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In the structure of **3**, the terminal methoxy moiety of the C(9)-based $CH_2CH_2OCH_3$ arm of the dithiocarbamate ligand was found to be disordered. (Though there is some evidence that there is a small amount of disorder of the whole of the dithiocarbamate ligand, this only becomes significant at the O(11)–C(12) unit.) Two partial occupancy orientations were identified for the O(11)–C(12) unit of *ca.* 90 and 10% occupancy. The geometries of the two orientations were optimised, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically. The PF_6 counteranion was found to be disordered. Two complete orientations were identified of *ca.* 87 and 13% occupancy. The geometries of the two orientations were optimised and only the atoms of the major occupancy orientation were refined anisotropically.

The C(15)-based terminal tolyl moiety in the structure of **15** was found to be disordered. Two partial occupancy orientations were identified of *ca.* 67 and 33% occupancy. The geometries of the two orientations were optimised and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically. Part of both of the $CH_2CH_2OCH_3$ arms of the dithiocarbamate ligand were found to be disordered. For the C(5)-based arm, two partial occupancy orientations for the terminal O(7)–C(8) unit were identified of *ca.* 86 and 14% occupancy. For the C(9)-based arm, three partial occupancy orientations for the terminal C(10)–O(11)–C(12) unit were identified of *ca.* 57, 35 and 8% occupancy. In each case, the geometries of the orientations were optimised and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically. Though not disordered, the included 30% occupancy dichloromethane solvent molecule occupies a site adjacent to the 35% occupancy orientation of the C(10)–O(11)–C(12) unit and, by virtue of the centre of symmetry, adjacent to the other two orientations of this unit as well. However, the relative occupancies of all these units are such that no "impossible" contacts need ever be present.

Fig. S1 The molecular structure of the cation in **3** (30% probability ellipsoids).

Fig. S2 The molecular structure of **15** (50% probability ellipsoids).

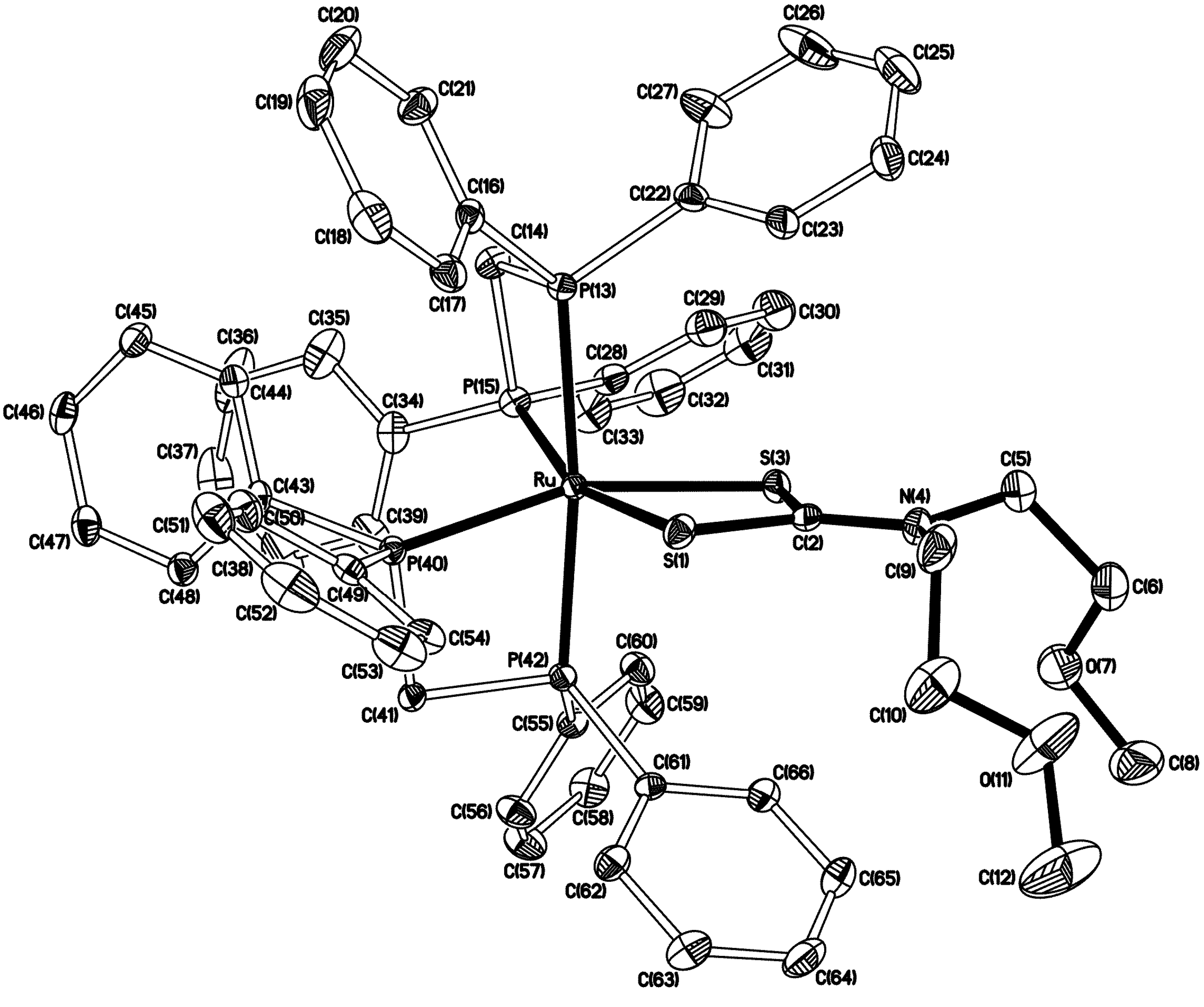

Fig. S1

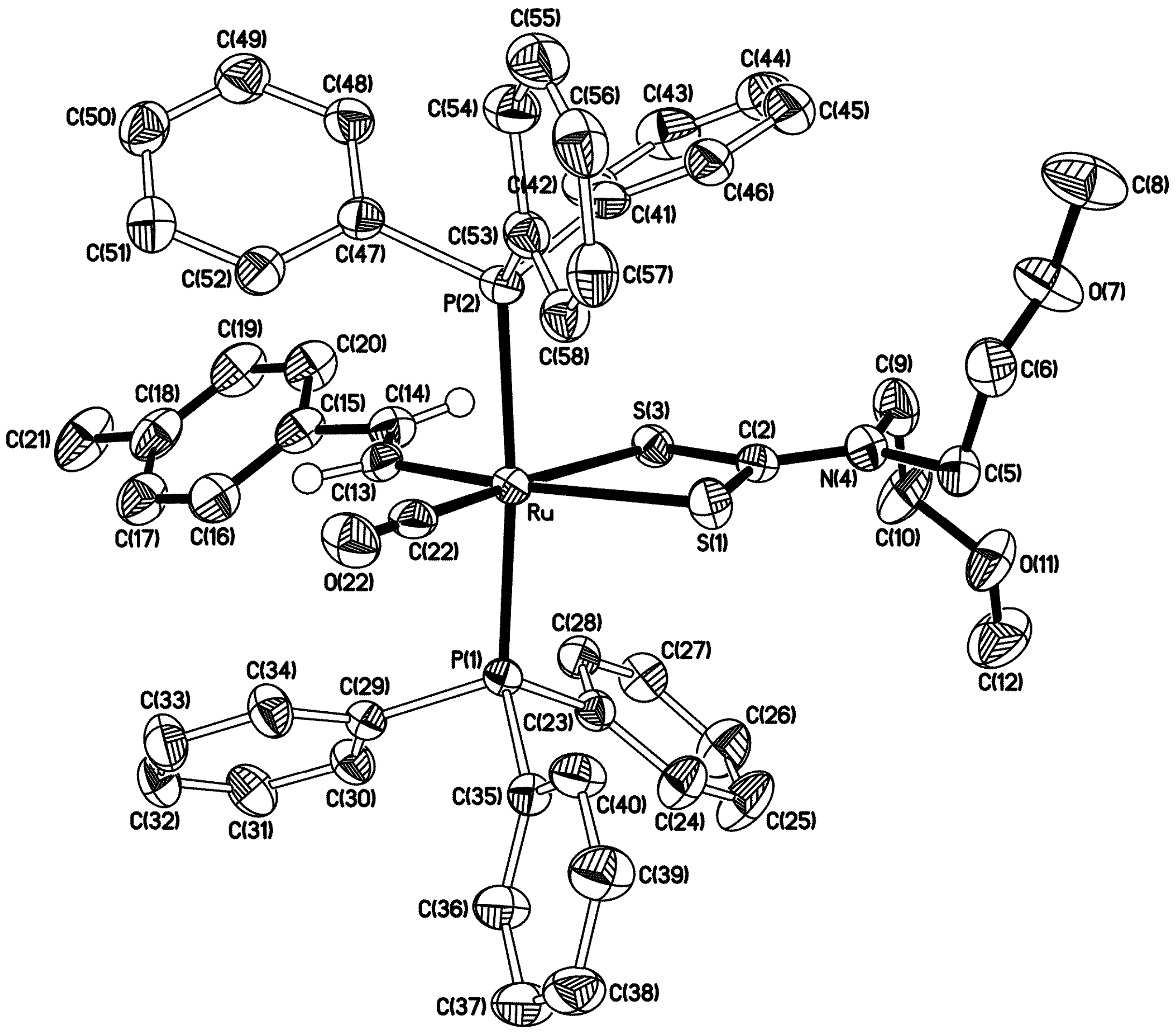
C(55)
C(49)
C(44)
C(48)
C(56)
C(43)
C(50)
C(54)
C(45)
C(42)
C(46)
C(41)
C(8)
C(51)
C(53)
C(47)
C(52)
C(57)
P(2)
O(7)
C(58)
C(19)
C(20)
C(9)
C(6)
C(18)
C(15)
C(14)
S(3)
C(2)
C(21)
N(4)
C(5)
C(13)
Ru
C(17)
C(16)
C(22)
S(1)
C(10)
O(11)
O(22)
C(28)
C(27)
P(1)
C(12)
C(34)
C(33)
C(29)
C(26)
C(23)
C(35)
C(40)
C(30)
C(32)
C(31)
C(24)
C(25)
C(39)
C(36)
C(37)
C(38)

Fig. S2