

## Supporting Information — X-Ray Crystallography

**Manuscript:** Multifunctional dithiocarbamates: Synthesis and ring-closing metathesis of diallyldithiocarbamate complexes

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### The X-ray crystal structure of **3**

The included dichloromethane molecule in the structure of **3** was found to be disordered. Two partial occupancy orientations of *ca.* 76 and 24% occupancy were identified, their geometries optimised, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically.

### The X-ray crystal structure of **5**

The diffraction data for crystals of **5** clearly revealed twinning problems, and unfortunately we were unable to isolate a single crystal. As all our attempts to grow better crystals failed, a data set was collected using the best of the crystals available in the hope that in the data processing stage an adequate model for the twinning could be found. Using the data set that was collected, various attempts were made to model the twinning, but unfortunately, none of these were particularly successful. The “best” approach actually involved not modelling the twinning at all; *ca.* 71% of the 13216 identified peaks fitted to the *ca.* 8150 Å<sup>3</sup> unit cell, and processing the data using just this cell led to a data set with an  $R_{\text{int}}$  of *ca.* 3%. (The attempts to model the twinning invariably led to data sets where the  $R_{\text{int}}$  was in excess of 20%.)

The solution and refinement of this data set using the most likely space group,  $C2/c$ , understandably resulted in a somewhat high final  $R$ -factor (*ca.* 11%). Attempts using the lower symmetry non-centrosymmetric space groups  $C2$  and  $Cc$  both resulted in lower  $R$ -factors (as one would expect) with two independent complex cations, anions and solvent molecules. In each case the pairs of cations, anions and solvent molecules looked to be centrosymmetrically arranged (again as one would expect given that using  $C2/c$  worked reasonably well), but the thermal parameters of many of the atoms were badly behaved (many went non-positive definite) and the absolute structure parameter refined to *ca.* 0.5. These signs clearly suggest that the  $C2/c$  approach is the most sensible one, and so that was the one we retained.

## The X-ray crystal structure of **15**

The structure of **15** was found to contain two independent cationic complexes (**A** and **B**), two independent PF<sub>6</sub> anions, and four unique chloroform sites (three in general positions and one adjacent to a centre of symmetry). One of the PF<sub>6</sub> anions [that based on P(20)] was found to be disordered. Three partial occupancy orientations were identified of *ca.* 39, 32 and 29% occupancy. The geometry of each orientation was optimised, and all three orientations were refined isotropically. Two of the three general position chloroform sites [those based on C(50) and C(60)] were found to be disordered, as was the chloroform position adjacent to a centre of symmetry [based on C(70)]. For both the C(50) and C(60)-based molecules, three partial occupancy orientations were identified, with occupancies of *ca.* 66, 18 and 16% for C(50), and *ca.* 72, 16 and 12% for C(60). The geometry of each orientation was optimised, and in each case only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically. For the C(70)-based molecule, (which must be  $\leq 50\%$  occupancy because of the adjacent centre of symmetry) three partial occupancy orientations were identified, with occupancies of *ca.* 23, 14 and 13% (a further three orientations with the same occupancies are related to these by the centre of symmetry). The geometry of each orientation was optimised, and all three orientations were refined isotropically.

## Discussion of the data for the dithiocarbamate unit

In the structure of compound **3**, the equatorial plane formed by the metal and the donor atoms of the dithiocarbamate, alkenyl and carbonyl ligands is flat, the Ru, S(1), S(3), C(11) and C(20) atoms being coplanar to within *ca.* 0.02 Å. The dithiocarbamate unit is only slightly distorted from planarity [the dihedral angle across the C(2)–N(4) bond is *ca.* 3°], but it is noticeably inclined to the equatorial plane, there being a *ca.* 8° fold about the S(1)⋯S(3) vector such that N(4) lies *ca.* 0.36 Å out of the equatorial plane in the direction of P(1).

In compound **5** the dithiocarbamate unit is more distorted from planarity than was the case in **3**, with the dihedral angle across the C(2)–N(4) bond being around 9° compared to *ca.* 3° in **3**. However, in common with **3** there is again a significant fold about the S⋯S vector of *ca.* 9° (compared to approximately 8° in **3**) and, in combination with S(1) lying so far out of the coordination plane, this results in N(4) lying around 0.93 Å out of the {Ni,S(3),P(11),P(15)} plane in the direction of C(6).

In contrast to the distortions of the dithiocarbamate ligand seen in the structures of **3** and **5**, the C(2)–N(4) torsion angle in [Ni(S<sub>2</sub>CNC<sub>4</sub>H<sub>6</sub>)(dppp)]PF<sub>6</sub> (**15**) is near zero (*ca.* 0.2 and

0.4° in A and B respectively), but at the same time the fold about the S...S vector is significantly increased to ca. 16° in both A and B. The result is that N(4) lies ca. 0.76 Å [0.72 Å] “above” the {Ni,S(1),S(3),P(9)} plane (with regards to the view shown in Fig. 4).

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

**Fig. S2** The molecular structure of the cation present in the crystals of **5** (50% probability ellipsoids).

**Fig. S3** The molecular structure of one (**A**) of the two crystallographically independent cationic complexes present in the crystals of **15** (50% probability ellipsoids).

**Fig. S4** The molecular structure of one (**B**) of the two crystallographically independent cationic complexes present in the crystals of **15**.

**Fig. S5** The molecular structure of one (**B**) of the two crystallographically independent cationic complexes present in the crystals of **15** (50% probability ellipsoids).

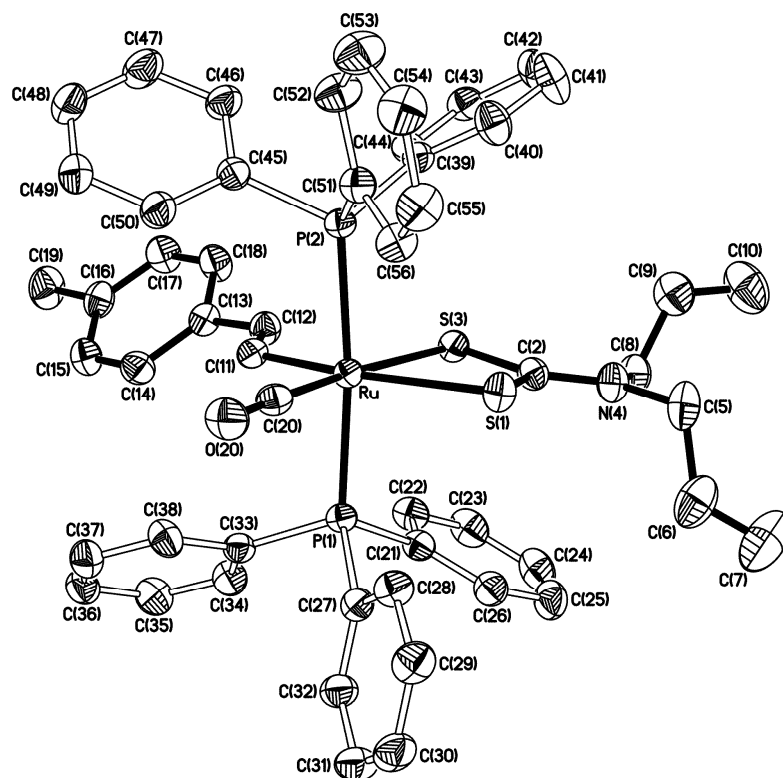


Fig. S1

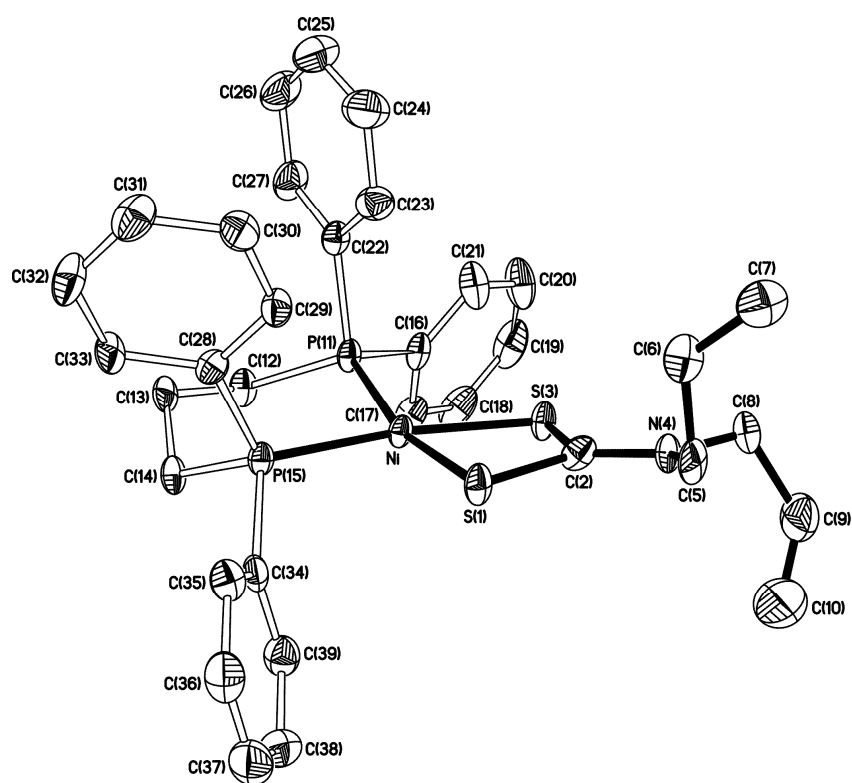


Fig. S2

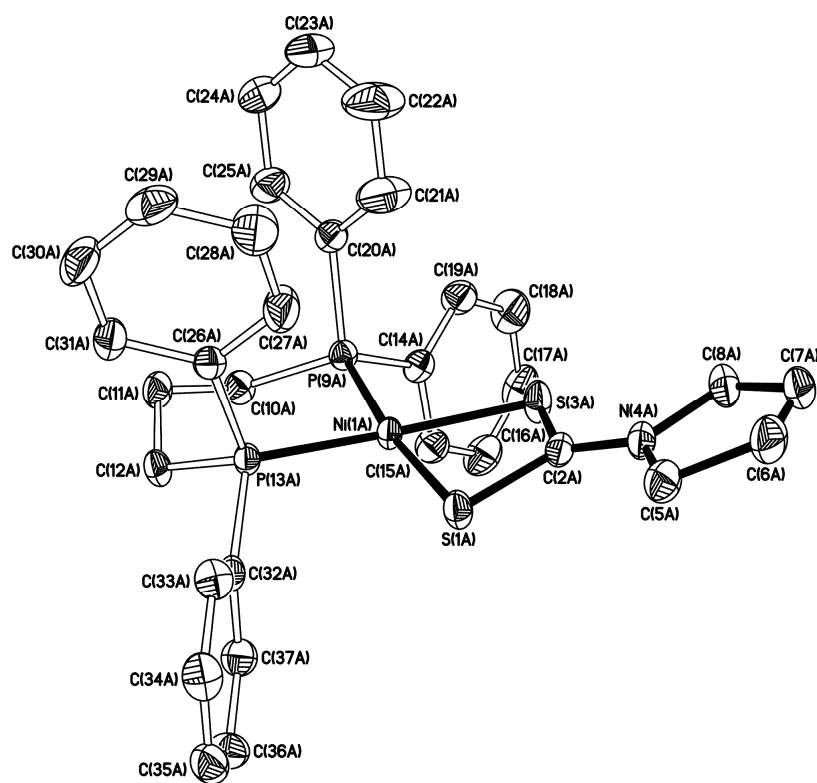


Fig. S3

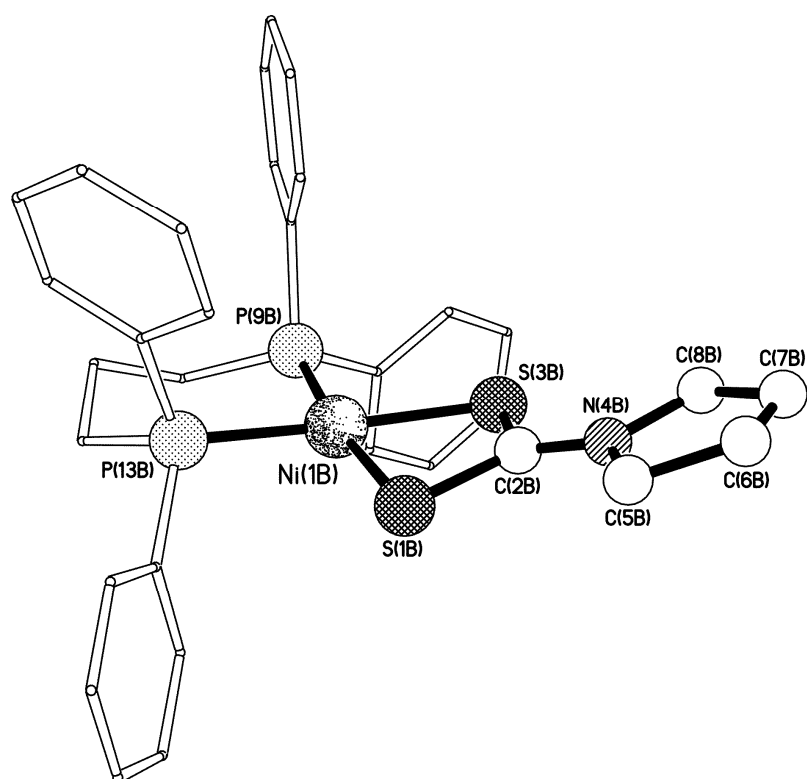


Fig. S4

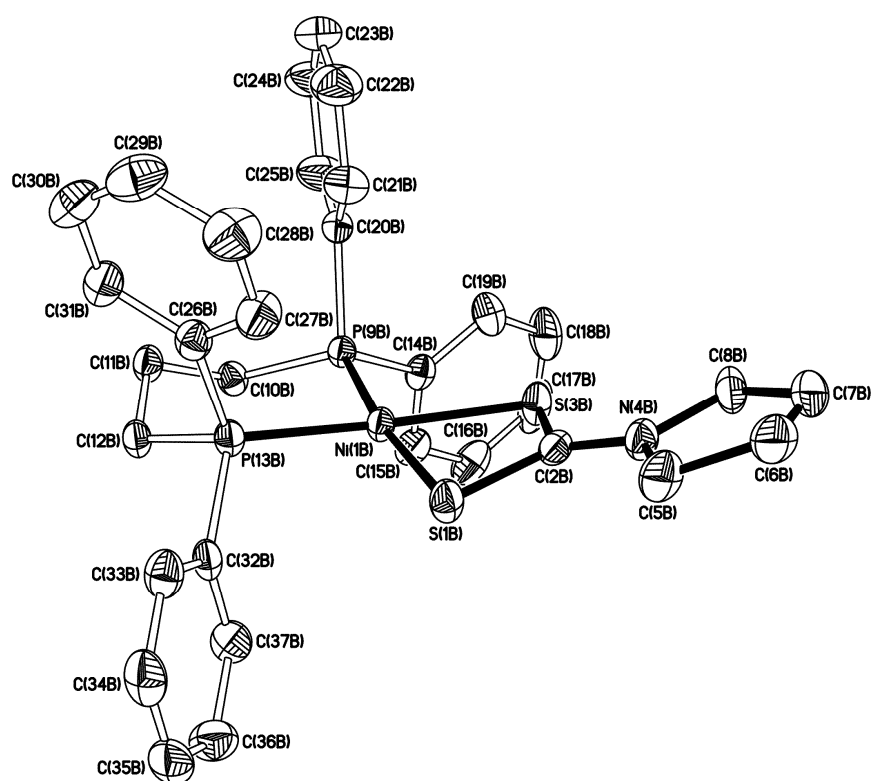


Fig. S5