

Rh–POP Pincer Xantphos Complexes for C–S and C–H Activation. Implications for Carbothiolation Catalysis.

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Supporting Materials

Details of structural refinements for the crystallographically characterized complexes. Full details of the data collection, refinement parameters and bond lengths and angles can be found in the accompanying CIFs.

Solid–state structure of complex **12**.

Compound **2d** (CCDC 1025603)

Crystals were obtained directly from a C₆H₅Cl solution of **2d**

Several of the CF₃ groups were disordered and modelled over two sites and restrained to maintain sensible geometries. A chlorobenzene molecule was located in the fourier map and was modelled over two positions and their occupancies refined to 50% each. The chlorine-carbon bondlengths of the solvent chlorobenzene were fixed to 1.76 Å.

Compound **5** (CCDC 1025604)

Large yellow crystals were grown from benzene/pentane

Compound **6** (CCDC 1025605)

Orange crystals were grown from dichloromethane/pentane

Two of the CF₃ groups were disordered and modelled over two sites and restrained to maintain sensible geometries.

Compound **7** (CCDC 1025606)

Yellow/orange crystals were grown from dichloromethane/pentane

Four strong peaks were located in the fourier map and assigned as the chlorines in two dichloromethane molecules with approximately 50% occupancy each. Two dichloromethane molecules were refined in these positions with similarity restraints used to maintain sensible geometries. The resulting C-Cl bond lengths are fully consistent with reported dichloromethane geometries. Due to the presence of this disorder the Rh-Cl bond lengths may not be reliable. Several of the CF₃ groups upon the anion were modelled over two positions and restrained to maintain sensible geometries.

Compound mer-**8** (CCDC 1025607)

Orange crystals were grown from 1,2-C₆H₄F₂/pentane

Several of the CF₃ groups were disordered and modelled over two sites and restrained to maintain sensible geometries. A difluorobenzene molecule was located in the fourier map and was modelled over two positions and their occupancies refined to 50% each. Also a pentane molecule was located in the fourier map and it was restrained to maintain sensible geometries.

Compound **10** (CCDC 1025608).

Brown crystals were grown from difluorobenzene/pentane

A disordered solvent molecule was located in the fourier map, since this could not be adequately modelled as difluorobenzene or pentane the structure was treated using the SQUEEZE algorithm leaving a void from which the electron density was removed. Several of the CF₃ groups were disordered and modelled over two sites. Similarity restraints were employed to maintain sensible geometries.

Compound 11.(CCDC 1025609)

Orange plate crystals were grown from fluorobenzene/pentane

Upon initial refinement it became clear that the cation existed in two disorder positions. The electron density peaks above and below the rhodium corresponding mainly to the sulphur atom are of equal intensity. The SMe and C₆H₄(COC₂H₄N) groups were modelled over two sites and similarity restraints were used to maintain sensible geometries. The occupancies of the two disorder components refined to approximately 50% each. Twinning was examined as a possibility but sensible twin laws refined to zero occupancy. A fluorobenzene molecule was located in the fourier map which is disordered over a symmetry element. This solvent molecule refined to 40% occupancy suggesting incomplete incorporation of the solvent within the crystalline phase. Several of the CF₃ groups upon the anion were modelled over two positions and restrained to maintain sensible geometries. Upon completion of the structure residual electron density was located next to the rhodium and sulphur atoms, this is expected to be a minor disorder component of the cation with a secondary rhodium position, this component was not modelled. The coordination geometry of the oxazoline group could occur through the N or O atom, by crystallography it is difficult to tell which position is coordinating. The structure is modelled with the N atom coordinating to rhodium, which is believed to be the more likely case. However exchange of the N and O atoms at the end of refinement does not greatly effect the thermal ellipsoids or R factor (R = 6.98% turns to R = 7.02%). It is possible that either coordination mode is occurring or even a disordered mixture.

Compound 12 (CCDC 1025610)

Yellow/orange crystals were grown from chlorobenzene/toluene/pentane. Upon extraction from the solvent the crystals cracked up within a couple of minutes. Bubbles were observed in the polyfluoroether oil in which the crystals were placed into. This is expected to be due to loss of solvent from the crystalline phase when removed from the parent solution.

Upon initial refinement it became clear that the cation existed in two disorder positions. The electron density peaks above and below the rhodium corresponding mainly to the sulphur atom are of equal intensity. The SMe and C₆H₄(C₅H₄N) groups were modelled over two sites and similarity restraints were used to maintain sensible geometries. The occupancies of the two disorder components refined to approximately 50% each. A disordered solvent molecule was located in the fourier map, since this

could not be adequately modelled as chlorobenzene, toluene or pentane the structure was treated using the SQUEEZE algorithm leaving a void from which the electron density was removed. Several of the CF₃ groups upon the anion were modelled over two positions and restrained to maintain sensible geometries. One side of the phosphine ligand was also disordered, possibly in correlation with the C₆H₄(C₅H₄N) disorder component. The phosphorus atom and phenyl groups were initially modelled over two positions and their occupancies refined to approximately 50% each. Upon further investigation of the fourier map a third position of one phenyl group was located and one disorder group split into two smaller occupancy fragments. Due to this extensive disorder the structure struggled to converge and a max shift of less than 0.6 was not achieved even after 3500 refinements

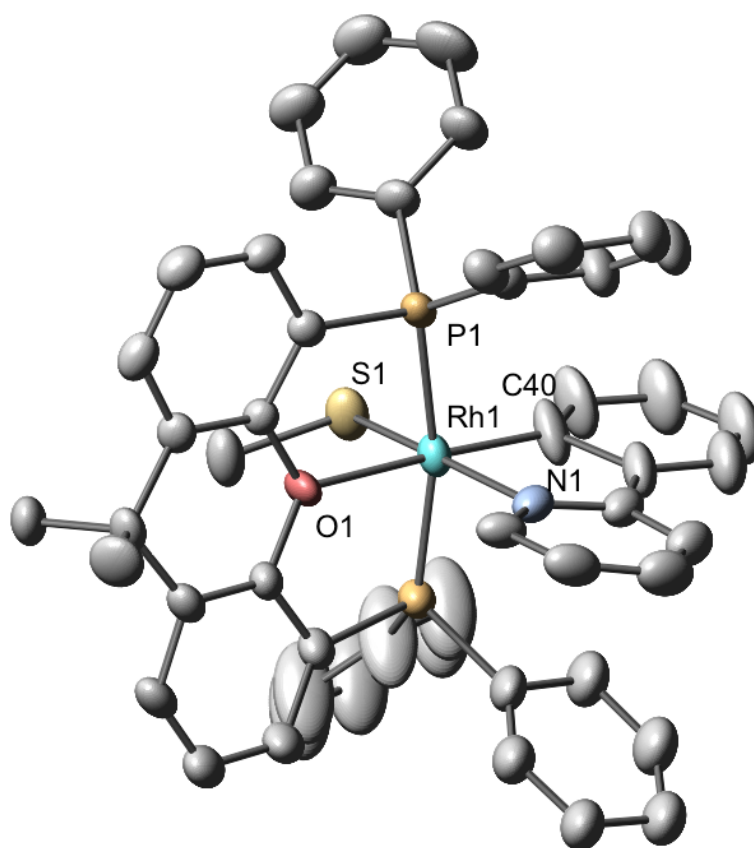


Figure S1. Solid-State structure of complex **12** showing the cation only. Hydrogen atoms are not shown. Only one disordered component is shown. See CIF for full details. Displacement ellipsoids are presented at the 50% probability level.

Compound 13.(CCDC 1025611)

Turquoise crystals were grown from dichloromethane/pentane

The hydrogen atoms upon the allyl ligand were located upon the fourier map and refined freely before applying the riding model to complete refinement. Several of the CF₃ groups upon the anion were modelled over two positions and restrained to maintain sensible geometries.

The hydrides were placed in calculated positions with a sensible bondlength of 1.5 Å. Refinement of these positions resulted in unsuitable Rh-H bond lengths and so was avoided

Compound 14 (CCDC 1025612)

Small colourless crystals were grown from chlorobenzene/pentane

The hydride was placed in a calculated position with a sensible bondlength of 1.5 Å. Refinement of this position resulted in an unsuitable Rh-H bond length and so was avoided. One molecule of chlorobenzene solvent is also located in the crystal structure