# Supporting Information

## Aluminium Complexes with Thio-Phosphorus Ligands: Syntheses and Characterisations of [Al(CyPS$_3$)(CyPHS$_2$)] and [Al(S$_2$PPh$_2$)$_3$]

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## X-ray Crystallography

The P–H proton in the structure of **1** was located from a $\Delta F$ map and refined freely. The included toluene solvent molecule was found to be disordered about a centre of symmetry, and so the occupancies of all of the atoms were set at 50%. The phenyl ring was optimised, and all of the non-hydrogen atoms were refined anisotropically.

The crystals of **3** were found to be severely twinned, and no single crystal was located. Complete data sets were collected for two different crystals, and the results presented in this paper are from the second crystal, with the collected images having been reduced based on a two component twin model with five kinds of peak overlap (and hence the final hkl file contains more data than would otherwise be the case). The structure was found to contain four independent complexes (**3-I** based on Al, **3-II** based on Al', **3-III** based on Al", and **3-IV** based on Al*), two of which (**3-III** and **3-IV**) have disordered phenyl rings. In **3-III**, the C(1") and C(19") rings were found to be disordered, and in each case two orientations were identified. Whilst the occupancies of the two orientations for the C(1") were allowed to refine freely (ending at a *ca.* 54:46 ratio), due to close intermolecular "contacts" the occupancies of the two orientations at C(19") had to be fixed at exactly 50:50 (at any other ratio there would inevitably sometimes be a situation were two rings co-exist when they could not physically both be present). In complex **3-IV** disorder was found at the C(1*), C(25*) and C(31*) phenyl rings, and in each case two orientations for the phenyls rings were identified. The occupancies at C(1*) were allowed to refine freely, and settled at *ca.* 60:40. In order to preserve sensible C–P–C angles at P(3*), the disorders at C(25*) and C(31*) were treated as linked, meaning that the disorder ratios would have to be the same. Due to close intermolecular "contacts", the disorder ratio at C(31*) had to be fixed at 50:50, and so that at C(25*) also had to be fixed at 50:50. However, sensible C–P–C angles at P(3*) are only achieved if one assumes that C(25*) co-exists only with C(31*), and C(25D) likewise with C(31D) [C(25D) and C(31D) being the parent atoms of the second orientations of the C(25*) and C(31*) phenyl rings]. Throughout all four complexes present in **3**, all of the phenyl rings were refined as optimised rigid bodies, and all of the major occupancy (*i.e.* 50% or greater) non-hydrogen atoms were refined anisotropically. Distance restraints were applied for all of the 1,2 and 1,3 P–C distances for the disordered phenyl rings, making them all the same as each other, and thermal parameter similarity restraints were applied for all the carbon atoms involved. For a number of the carbon atoms, spherical thermal parameter restraints had to be applied to prevent their thermal parameters from going non-positive definite.

**Fig. S1** The molecular structure of **1** (50% probability ellipsoids).

**Fig. S2** The molecular structure of **2** (50% probability ellipsoids).

**Fig. S3** The molecular structure of one (**3-I**) of the four crystallographically independent complexes present in the crystals of **3** (50% probability ellipsoids).

**Fig. S4** The molecular structure of one (**3-II**) of the four crystallographically independent complexes present in the crystals of **3**.

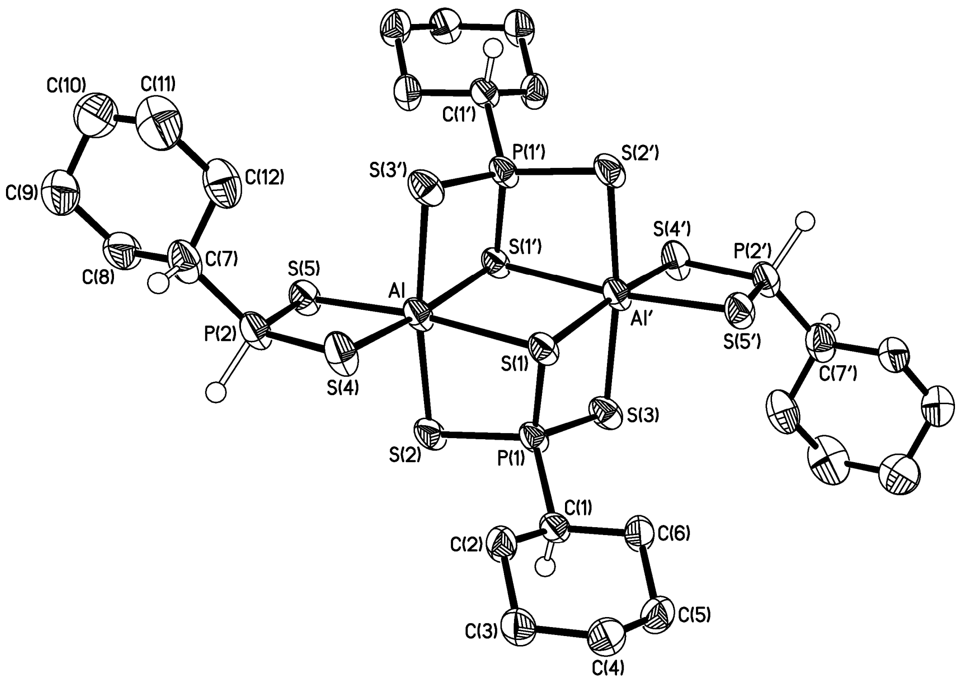
**Fig. S5** The molecular structure of one (**3-II**) of the four crystallographically independent complexes present in the crystals of **3** (50% probability ellipsoids).

**Fig. S6** The molecular structure of one (**3-III**) of the four crystallographically independent complexes present in the crystals of **3**.

**Fig. S7** The molecular structure of one (**3-III**) of the four crystallographically independent complexes present in the crystals of **3** (50% probability ellipsoids).

**Fig. S8** The molecular structure of one (**3-IV**) of the four crystallographically independent complexes present in the crystals of **3**.

**Fig. S9** The molecular structure of one (**3-IV**) of the four crystallographically independent complexes present in the crystals of **3** (50% probability ellipsoids).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C(9)
C(8)
C(7)
S(5)
P(2)
S(4)
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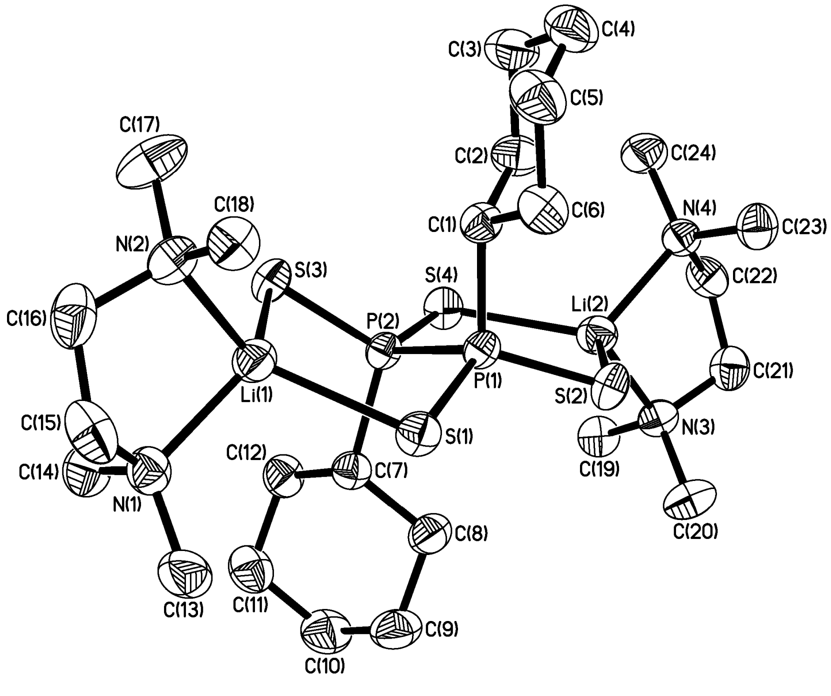
C(1′)
P(1′)
S(2′)
S(1′)
S(4′)
P(2′)
Al′
S(5′)
S(1)
C(7′)
S(2)
P(1)
S(3)
C(1)
C(2)
C(6)
C(3)
C(5)
C(4)

Fig. S1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Li(2)
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P(1)
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S(1)
N(3)
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C(7)
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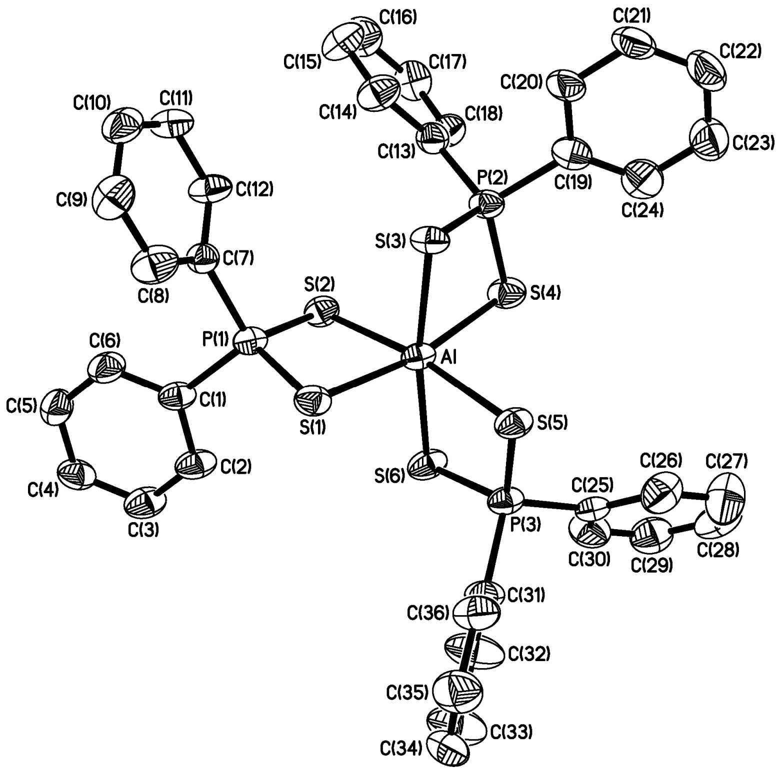
C(10)

Fig. S2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C(19)
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S(3)
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C(8)
S(2)
S(4)
C(6)
P(1)
Al
C(5)
C(1)
S(1)
S(5)
C(2)
S(6)
C(26)
C(27)
C(4)
C(25)
C(3)
P(3)
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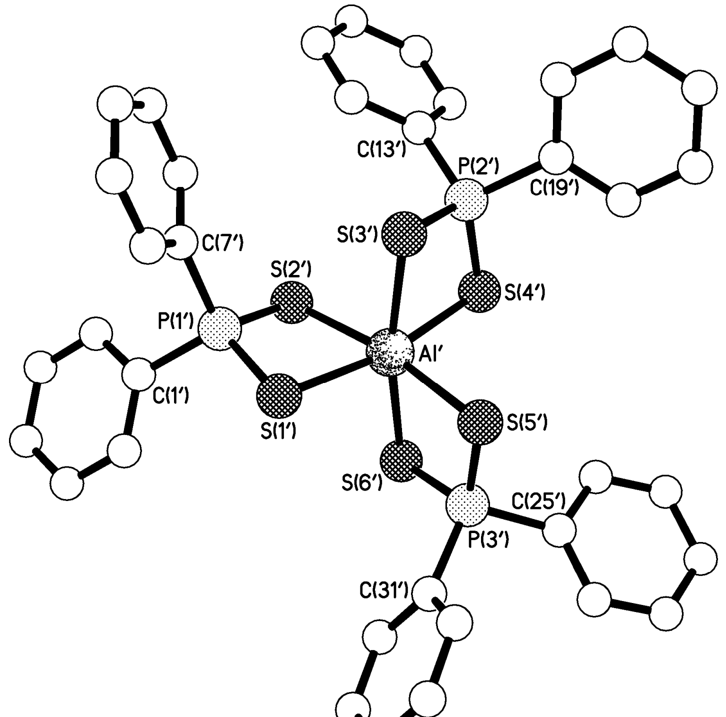
C(33)
C(34)

Fig. S3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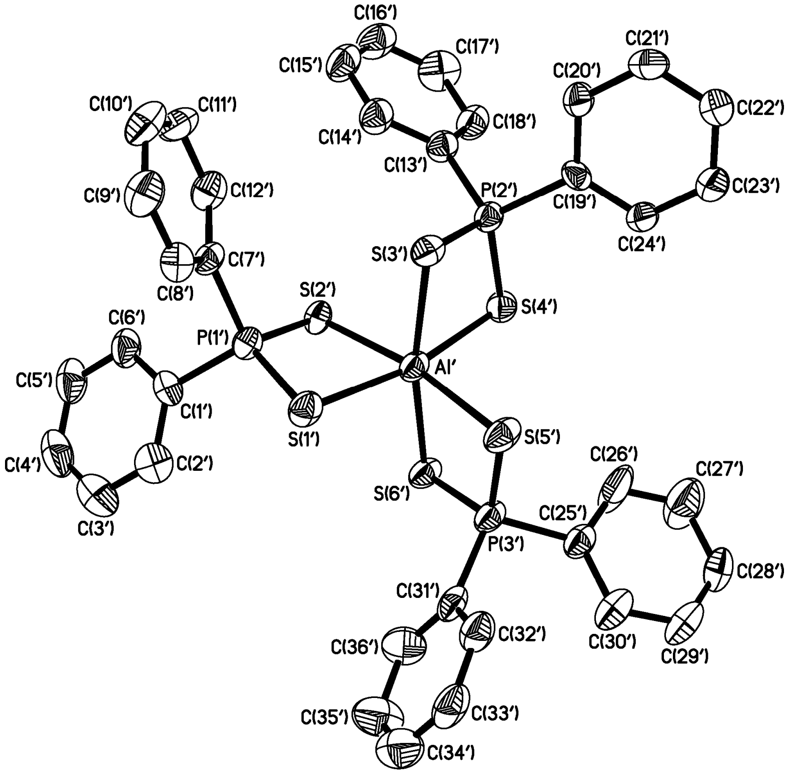
S(1′)
S(5′)
S(6′)
C(25′)
P(3′)
C(31′)

Fig. S4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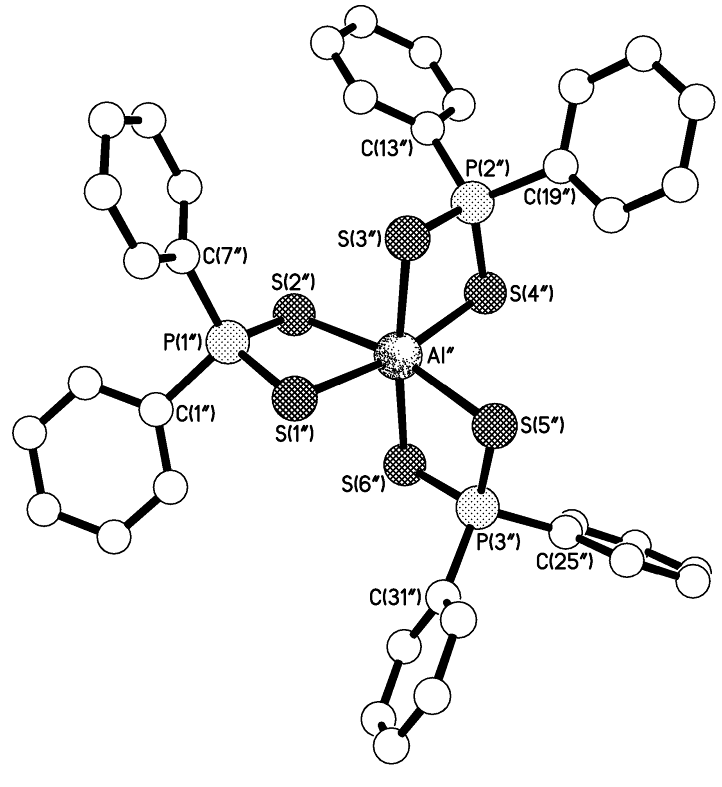
C(34′)

Fig. S5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S(1″)
S(5″)
S(6″)
P(3″)
C(25″)
C(31″)

Fig. S6

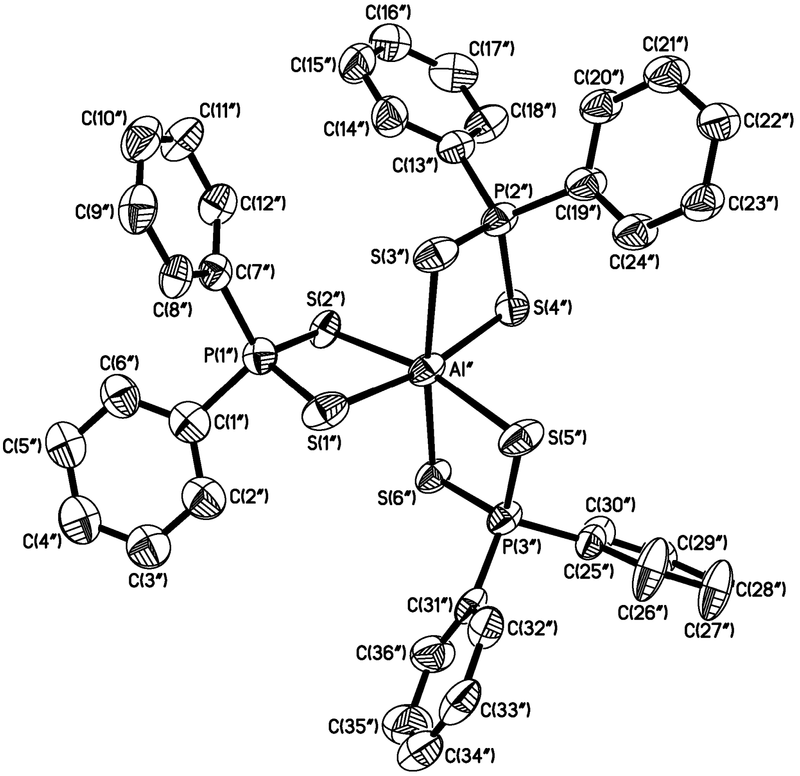
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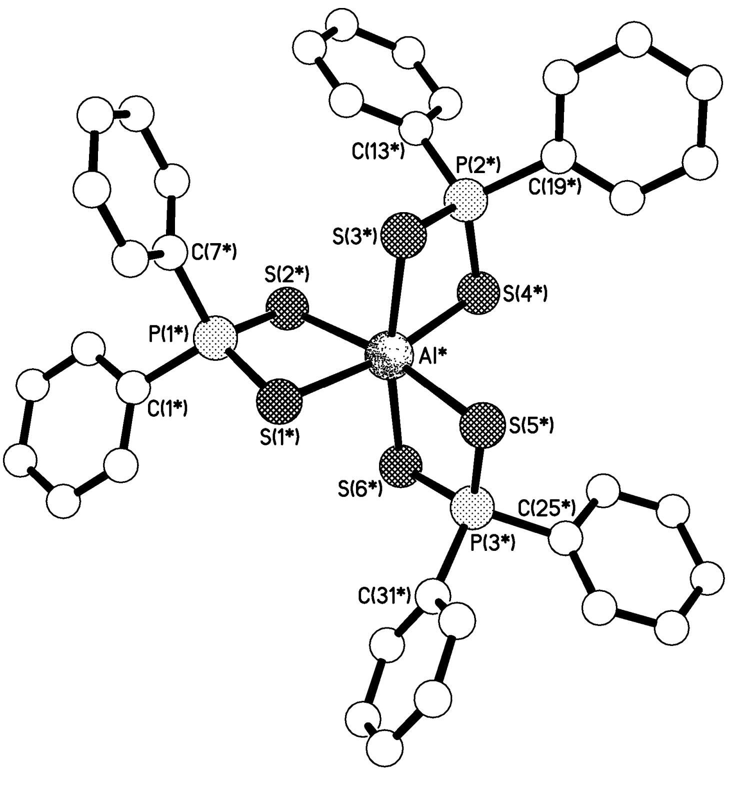
Fig. S7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S(3*)
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S(4*)
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S(1*)
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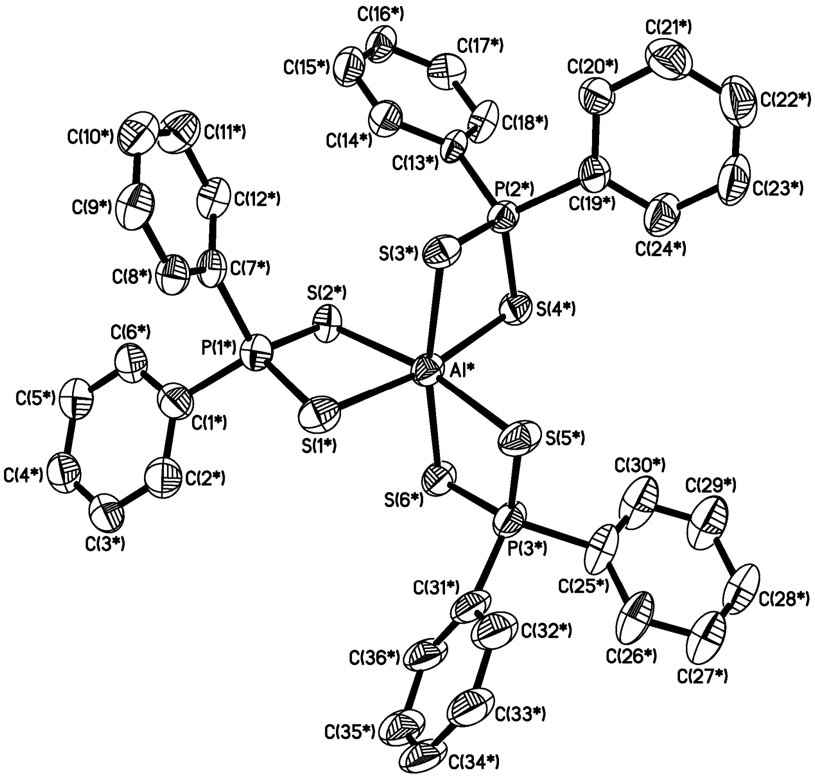
S(6*)
C(25*)
P(3*)
C(31*)

Fig. S8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C(34*)

Fig. S9