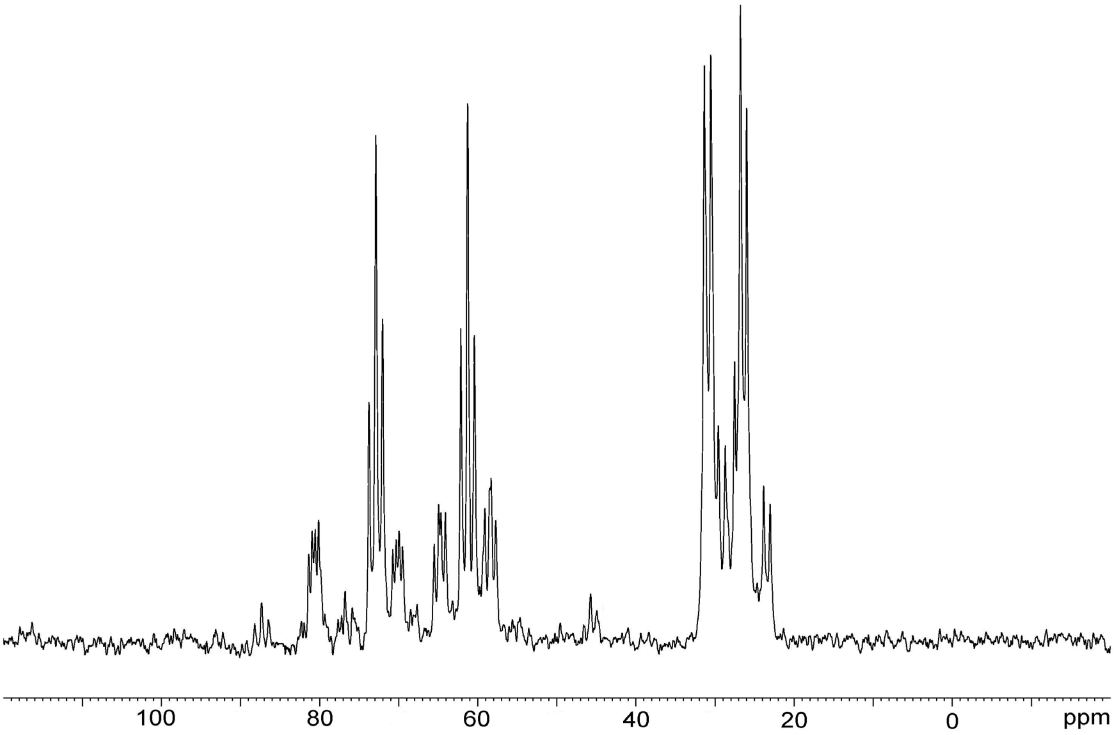

Figure 1. ^{31}P NMR spectrum of complex **9** at 180 K in d^{8}-toluene

X-ray Crystallography refinement details

Complex 2. The main residue is well-ordered and all non-hydrogen atoms were refined anisotropically. The structure contains two lattice molecules of benzene, one of which lies on an inversion centre and is well-ordered, C50-C52A. Geometric restraints were applied to obtain reasonable aromatic C-C distances. The second molecule of benzene is disordered and was modeled over two sites using geometric restraints. The thermal parameters were best refined using an anisotropic 75:25 mixture.

Complex 4. The main residue is well-ordered and all non-hydrogen atoms were refined anisotropically, with the exception of carbon atoms C79-C81 from an *n*-butyl group. These were modeled over two sites using geometric restraints. The thermal parameters were refined best using a 75:25 isotropic mixture. The structure also contains a disordered lattice molecule of *n*-hexane which was modeled over two sites and the thermal parameters were optimally refined to an isotropic 70:30 mixture.

Complex 8. The complex crystallizes with two independent, chemically-equivalent molecules in the asymmetric unit and one ordered molecule of *n*-hexane, which lies on the inversion centre. Geometric restraints were applied to obtain reasonable C-C distances. The refinement was complicated by twinning of the data, stalling at R = 0.1260 and $wR2$ = 0.4161, with all atoms present and anisotropic. There were many signs of twinning, including an unusually large ratio of data to parameters and a significant number of high intensity bad reflections. Application of the twin determination program ROTAX (WinGX) showed that twinning occurred in a 180 ° rotation about the [1 -1 1] reciprocal lattice direction.[1] WinGX was used to prepare an HKLF5 file for further refinement.[2] Significant improvement in both R values, esds and background noise indicated that the correct twin law has been applied.

Complex 9. The complex contains a significant amount of disorder in the main residue which was also present when solved in the lower symmetry space group Cc. For this reason, the higher symmetry space group C2/*c* was chosen. The heavier atoms (Hg, S, P and N1 and N2) were refined with anisotropic displacement parameters. The phenyl ring located on P1, C1-C6, is disordered over two sites and the thermal parameters were refined best using a 60:40 isotropic mixture. The orientation of the phenyl ring and *n*-butyl group on P2, defining the absolute configuration of this chiral centre, is also disordered and the thermal parameters were refined best using a 60:40 isotropic mixture, suggesting the presence of both enantiomers in the solid-state structure. The second position of the *n*-butyl C31-C34 group is further disordered over two positions and is modelled as a 20:20 isotropic mixture. The *iso*-propyl group C16-C18 is also disordered over two sites and was modeled using a 50:50 isotropic mixture. A second position for the ligand S2-P3-N3-P4, including all carbon atoms, was found, with inversion of the chirality around P4 (disorder of the phenyl and *n*-butyl groups). The two positions were best refined as a 60:40 isotropic mixture. All carbon atoms on this ligand and N3 and N4 were refined isotropically. This structure also contains disordered molecules of solvent in the lattice, for which no reasonable model could be found. The data was treated with the program Squeeze (PLATON)[3] which helped improve the values of $R1$ and $wR2$ and the esds on all structural parameters. Details are given in the cif file of complex **9**.

1. R. I. Cooper, R. O. Gould, S. Parsons and D. J. Watkin, *J. Appl. Crystallogr.,* 2002, **35**, 168.
2. L. J. Farrugia, *J. Appl. Crystallogr.,* 1999, 32, 837.
3. A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool,* Utrecht University, Utrecht, The Netherlands, 2000.