

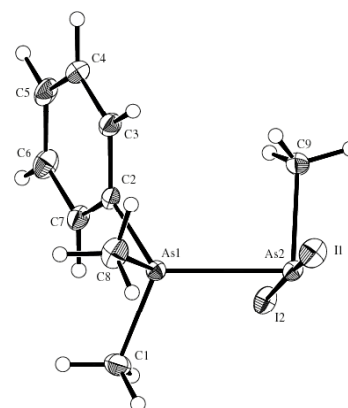
Coordination chemistry has merged with organic and organometallic chemistry and with catalysis with the result that there are now modifications available for nearly every standard reaction for converting achiral organic precursors into chiral products. Together with modern purification techniques, this has allowed the preparation – in a single step – of compounds in >98% enantiomeric purity for many reaction types. Work in this group is concerned with the synthesis of new types of chiral ligands, especially enantiomerically pure phosphines and arsines, for use as probes of inorganic stereochemistry, rearrangements in metal complexes, and as auxiliaries for asymmetric synthesis.



Heather Kitto and Rebecca Warr received grants from the Australian–German Joint Research Cooperation Scheme to work as exchange students in the University of Leipzig for one month (August). They visited en route to Leipzig the University of Cambridge and on the way home the Technical University Munich, where they presented lectures on their work in Canberra. Professor Wild accompanied the students on a grant funded by the Alexander von Humboldt Foundation. He presented a lecture in the University of Cambridge and an invited lecture at the INTAS Workshop 2003 on Phosphines, Chirality and Catalysis, which was held between 18–20 August in the University of Leipzig. Four postgraduate students from the University of Leipzig (Martina Hanner, Ulrike Helmstedt, Thomas Hoecher, and Uwe Polster) worked in the group for 1–3 months each during 2003 on grants funded by the Deutsche Akademischer Austausch Dienst (DAAD). Professor Wild was elected in April 2003 as a Fellow of the Australian Academy of Science.

### Burrows' Compounds Revisited

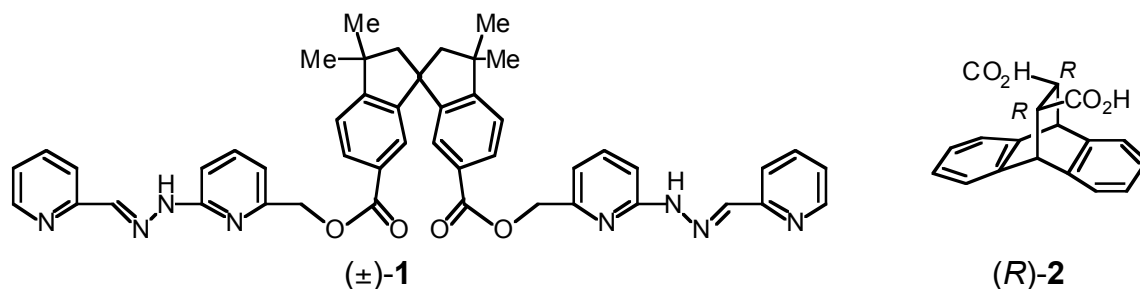
In connection with our investigations of tertiary phosphine and arsine-stabilised arsenium salts, we have synthesised the adducts  $\text{PhMe}_2\text{As}\cdot\text{AsI}_2\text{Me}$ ,  $\text{PhMeEtAs}\cdot\text{AsI}_2\text{Me}$  and  $\text{PhMe}_2\text{As}\cdot\text{AsI}_2\text{Ph}$ , which were first isolated by Burrows and Turner (*J. Chem. Soc.*, 1920, **117**, 1373). The crystal structures of the three compounds have been determined. The structure of  $\text{PhMe}_2\text{As}\cdot\text{AsI}_2\text{Me}$  is shown. In the structure, the  $\text{AsAsI}$  angles and the  $\text{AsAsC}$  angle of the iodoarsine are *ca.*  $90^\circ$ . Density functional theory calculations on the three structures are in agreement with the experimental data. (with S. Petrie, X. Zhou, and R. Stranger [Dept. Chemistry, ANU])



### Stereoselective Synthesis of Two-bladed Propeller Octahedral Metal Complexes

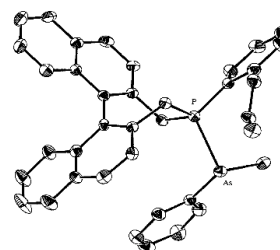
We have embarked on a program aimed at demonstrating that chiral metal complexes can be prepared by asymmetric synthesis – inorganic asymmetric synthesis. The approach being adopted is to transfer chiral information to a metal centre by means of an enantiomerically pure chiral auxiliary attached to appropriate chelating agents, as in ( $\pm$ )-**1**, with the auxiliary group subsequently being removed to leave the configurationally pure metal complex. Ligand ( $\pm$ )-**1** diastereoselectively complexes zinc(II) to produce a dizinc(II) helicate; the *S* enantiomer of the ligand generates two metal centres of  $\Delta$

configuration in the double-stranded helicate. Current work is concerned with the enantioselective synthesis of the analogous compound using the readily accessible chiral auxiliary (*R*)-**2**. (with R.J. Warr, A.C. Willis)



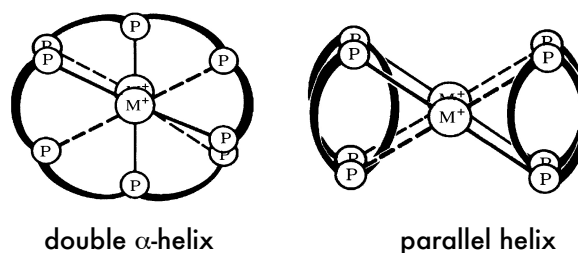
### Phosphine-Stabilised Arsenium Salts as Precursors for the Asymmetric Synthesis of Tertiary Arsines

Previous work has shown that the reaction of iodoarsines with tertiary phosphines in the presence of hexafluorophosphate ion gives adducts of the type  $[R_3P \rightarrow AsR^1R^2]PF_6$ , which react with carbanionic nucleophiles ( $Nu^-$ ) to give tertiary arsines  $(\pm)-AsR^1R^2Nu$ . Recently, a binaphthyl-substituted phosphepine has been identified as a very effective chiral auxiliary for the reaction, generating, via the arsenium adduct shown, arsines in enantiomeric excesses of up to 77%. This result is now being submitted to further testing, to define the conditions producing maximum stereoselectivity. (with E.H. Krenske, K.A. Porter, A.C. Willis)

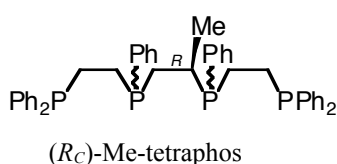


### Stabilisation of Double $\alpha$ -Helix Conformers of Dinuclear Metal Helicates Containing Tetra(tertiary phosphines)

Previous work in our laboratory has shown that (*S,S*)-tetraphos spontaneously self-assembles dinuclear metal helicates of the type  $(M)-[M_2\{(R,R)\text{-tetraphos}\}_2](PF_6)_2$  upon reaction with univalent silver and gold salts. These complexes have a double  $\alpha$ -helical or side-by-side parallel helix conformation



depending on the twist of the central 10-membered ring containing the two metal ions, which has the chiral twist-boat-chair-boat conformation. The ligand (*R<sub>C</sub>*)-Me-tetraphos is currently being synthesised by a novel route involving the ring-opening of a chiral phosphirane. Molecular modelling experiments have shown that the enantiomerically pure (*R<sub>P</sub>*,*R<sub>C</sub>*,*R<sub>P</sub>*) diastereomer of the phosphine will generate by stereoselective self-assembly the head-to-head diastereomer of the double  $\alpha$ -helix conformer of complexes of the type  $(P)-[M_2\{(S_P,R_C,S_P)\text{-tetraphos}\}_2](PF_6)_2$  (where  $M = Cu, Ag, Au$ ). A project has also begun on the metal templated synthesis of a tetrahedral phosphine-cage ligand. (with H. Kitto, K. Wells)



<http://rsc.anu.edu.au/research/wild.php>

