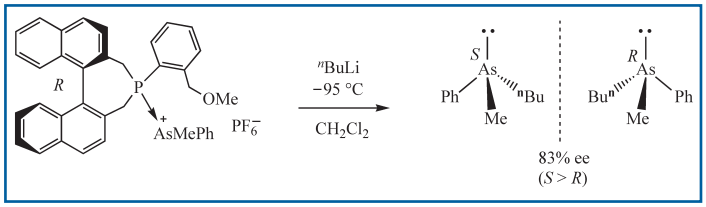
Inorganic Stereochemistry and Asymmetric Synthesis
Professor Bruce Wild

Coordination chemistry has merged with organic and organometallic chemistry and with catalysis such 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.

Elizabeth Krenske received a grant from the Australian–German Joint Research Cooperation Scheme to work as an exchange student in the University of Leipzig for one month (September). Elizabeth also visited the National University of Singapore, where she presented a lecture on her work.

Phosphine-stabilised Arsenium Salts and Their Use for the Asymmetric Synthesis of Tertiary Arsines

Our work on phosphine-stabilised arsenium salts has continued, with a fuller investigation of reactivity at the arsenium centre. We have carried out a detailed study of nucleophilic substitution reactions with organometallic nucleophiles, including organolithium, Grignard, and organozinc reagents. The synthetic route to the phosphine auxiliary has been improved, and it has enabled the preparation a range of optically active tertiary arsines in stereoselectivities ranging from 25% to 83%. For example, the reaction of the methylphenylarsenium adduct of the phosphine with ^{n}BuLi at –95 °C in dichloromethane leads to (*S*)-(*n*-butyl)methylphenylarsine in 83% enantiomeric excess. This work has been complemented by theoretical calculations for the stereochemical analysis of model adducts. *(With M L Coote, E H Krenske, K A Porter, A C Willis)*

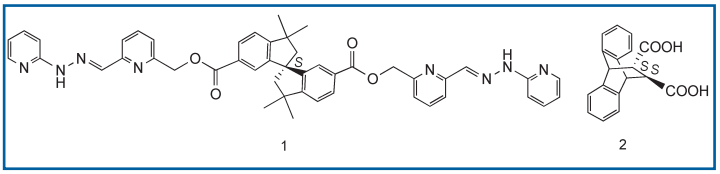


Macrocyclic Diphosphine-stabilised Diarsenium Salts

The bis(tertiary phosphine) $Ph_2PCH_2CH_2CH_2PPh_2$ (dppp) reacts with bis(iodophenylarsino)-1,2-ethane in dichloromethane in the presence of aq. NH_4PF_6 to give an 18-membered phosphine-stabilised tetra-arsenium salt, which has been characterised by X-ray crystallography. Treatment of the salt, which contains four chiral arsenium groups, with MeLi in –78 °C furnished (*R*,R**)-(±)/(*R*,S**)-$MePhAsCH_2CH_2AsMePh$ with liberation of the dppp. The diastereoselectivity of the reaction is negligible, but if the dppp is replaced by the enantiomerically pure diphosphine (*S,S*)-skewphos, the corresponding diphosphine-diarsenium complex affords, upon treatment with MeLi at –78 °C, the diarsine with the following stereoselectivities: (*R*,R**)-(±)/(*R*,S**) = 60:40 and (*R,R*):(*S,S*) = 60:40. The identities of the products and stereoselectivities of the reactions have been determined by complexation of the diarsine with enantiomerically pure (*S,S*)-$[Pt(OTf)_2\{1,2\text{-}C_6H_4(PMePh)_2\}]$ and analysis of the ^{31}P NMR spectrum of the resulting mixture of complexes. *(With A C Willis, X Zhou)*

Stereoselective Synthesis of Two-bladed Propeller Octahedral Metal Complexes

We have embarked on a project aimed at demonstrating that chiral metal complexes can be prepared by 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 1, with the auxiliary group subsequently being removed to leave the configurationally pure metal complex. Ligand 1 has been shown to diastereoselectively complex zinc(II) and iron(II) to produce dinuclear metal double α-helix helicates; the *S*-enantiomer of the ligand generating two metal centres of Δ-configuration. This is in contrast to the corresponding ligand containing the chiral auxiliary 2, which complexes iron(II) to produce a side-by-side helix helicate, the *S,S*-enantiomer of the ligand generating two metal centres of opposite configuration. *(With R J Warr, A C Willis, A D Rae)*



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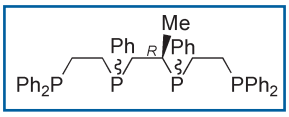
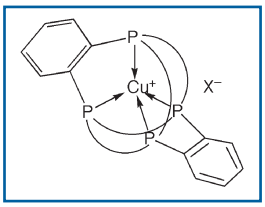
Stabilisation of Parallel and Double α-helix Conformers of Dinuclear Metal Helicates Containing Tetra(tertiary Phosphines)

The ligand (R_C)-Me-tetraphos has been synthesised from (*R*)-propane-1,2-ditriflate and appropriate phosphide reagents. The tetraphosphine has been isolated initially as a mixture of the borane adducts of the four possible diastereomers, chiral at carbon (*R*) and the two configurationally stable phosphorus stereocentres. One diastereomer of the mixture has been isolated by fractional crystallisation. A highly stereoselective synthesis of this diastereomer has also been achieved by stereospecific displacement of the triflate groups from (*R*)-propane-1,2-ditriflate with an enantiomerically enriched phosphide–borane reagent. Molecular modelling of the structures of the cations of the complexes $[M_2\{(R)\text{-Me-tetraphos}\}_2](PF_6)_2$ containing the various diastereomers of the tetraphosphine indicates that the ligand containing two inner-phosphorus stereocentres of *R*-configuration will stabilise the double α-helix conformer of a double-stranded dimetal helicate with univalent Group 11 ions. *(With H Kitto, A D Rae, A C Willis)*



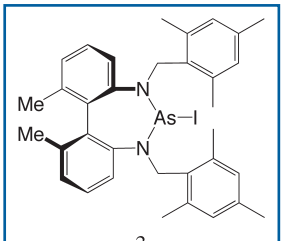
Tetrahedral Phosphine Cage Ligands and Complexes



Molecular modelling has indicated that it should be possible to synthesise a tetrahedral phosphine cage complex by the reaction of the appropriate 1,2-phenylenebis(alkenylphosphine)copper(I) complex with the analogous 1,2-phenylenebis(phosphine) complex under basic conditions. Current work is concerned with the synthesis and purification of the key starting materials 1,2-phenylenebis(dichlorophosphine) and 1,2-phenylenebis(phosphine) and their copper(I) complexes. *(With K Wells)*

Deracemisation of Chiral Arsines and Phosphines

Synthetic techniques for the production of chiral phosphines and arsines are presently limited by the necessity of resolution. Previous work within the group has identified the inversion of chiral phosphines in the presence of iodoarsines resulting in racemisation at equilibrium. Current research is focused on the synthesis of chiral iodoarsines to facilitate the deracemisation of phosphines of type 3. These will hopefully provide enantioenriched phosphines without the need for traditional resolution. *(With N L Kilah)*



3

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