

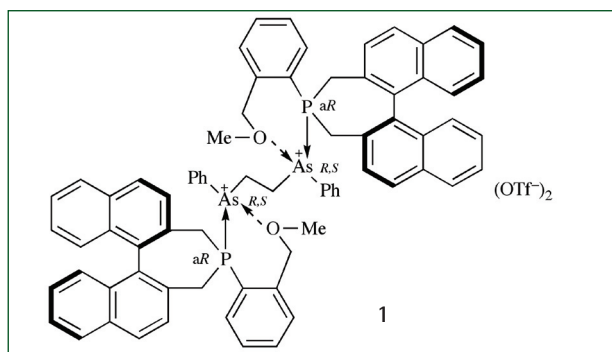


INORGANIC STEREOCHEMISTRY AND ASYMMETRIC SYNTHESIS

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.

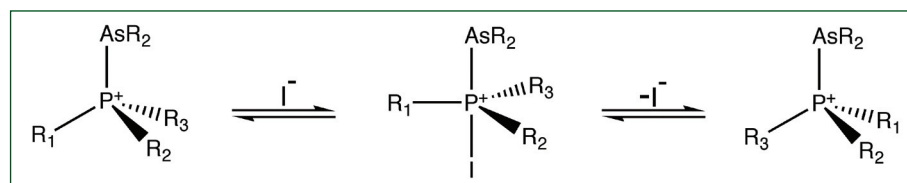
Phosphine-stabilised Arsenium Salts and the Asymmetric Synthesis of Tertiary Arsines



Our work in this area has been extended to the asymmetric synthesis of ditertiary arsines. Thus, the bis(*aR*)-phosphine-stabilised diarsenium salt **1** has been reacted at low temperature with *n*-butyllithium to give the (*S,S*)-bis(*n*-butylphenyl)diarsine in 88% enantioselectivity, along with 15% of the achiral (*R,S*) compound. The enantioselectivity of the reaction was determined by a novel NMR spectroscopic method involving the use of an enantiomerically pure diphosphineplatinum(II) group as the reference agent. This is the first asymmetric synthesis of a ditertiary arsine containing two chiral arsenic stereocentres. (With M L Coote, E H Krenske, A D Rae, M L Weir, A C Willis, X-T Zhou)

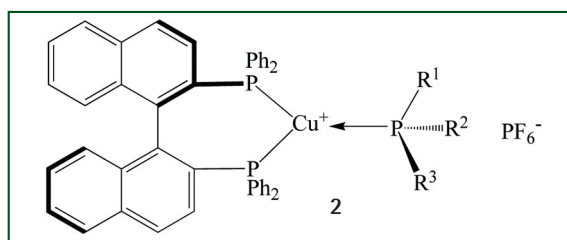
Deracemisation of Chiral Arsines and Phosphines via Asymmetric Transformation

Chiral phosphines are crucial for many industrial catalysts, but their resolutions are often time consuming and wasteful.



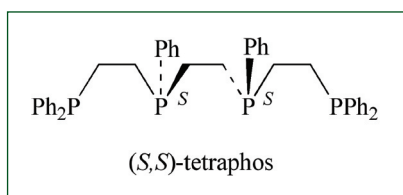
Pyramidal inversion at a phosphine centre results in racemisation, which has been observed for an enantiomerically pure phosphine in the presence of an iodoarsine.

If the arsenium ion is chiral, a shift in the equilibrium towards the most stable diastereomer of the adduct is conceivable via an asymmetric transformation. This deracemisation could allow the isolation of chiral phosphines without the need for traditional resolution. Initial investigations have focused on the synthesis of complexes derived from $[\text{Cu}(\text{R-BINAP})(\text{NCCH}_3)_2]\text{PF}_6$ with tertiary phosphines, viz. **2**. (With N L Kilah)



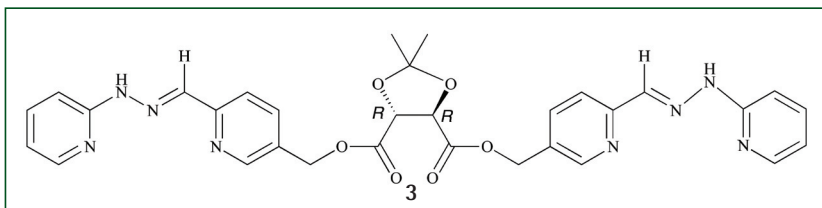
Polytertiary Phosphine Helicates

The self-assembly of molecules into large supramolecular structures is an important feature in biology and is now readily achieved in inorganic coordination chemistry with appropriate helical ligands and metal ions. Work in our laboratory has shown that (*S,S*)-tetraphos spontaneously self-assembles dinuclear metal helicates of the type of $(M)_2\{(R,R)\text{-tetraphos}\}_2(\text{PF}_6)_2$ upon reaction with univalent silver and gold salts and $(M)\text{-Pt}_2\{(R,R)\text{-tetraphos}\}_2(\text{OTf})_4$ upon reaction with $\text{Pt}(\text{COD})\text{Cl}_2$ in the presence of TMSOTf. The central 10-membered ring in each of these complexes has a chiral twist-boat-chair-boat conformation; the δ or λ twist of the ring generates a parallel or double α -helix conformer of the helicate. Current work is focused on the synthesis of similar complexes involving zero-valent metals and the synthesis of tetraphosphines with substituted backbones that will stabilise the double α -helix conformer of the helicate over that of the parallel helix conformer. (With H Kitto, A D Rae, A C Willis)



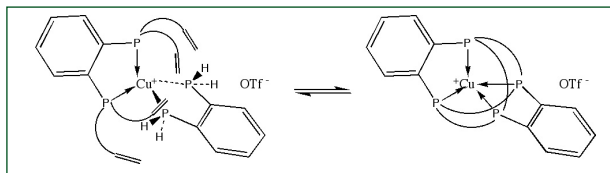
Asymmetric Synthesis of Two-bladed Propeller Octahedral Metal Complexes

We have embarked on a project aimed at demonstrating that single enantiomers of chiral metal complexes can be prepared by inorganic asymmetric synthesis. The approach being adopted is to transfer chiral information from an auxiliary attached to



appropriate chelating groups, as in **3**, with the auxiliary subsequently being removed to leave the configurationally pure metal complex. For this method to be successful, the product must have sufficient chemical and configurational stability to observe the single enantiomer of the complex produced. For these reasons, we have chosen as targets two-bladed propeller complexes of the type $(\pm)\text{-}[M(\text{PAPHY})_2]\text{X}_2$ and $(\pm)\text{-}[M(\text{PAPY})_2]$, which are available for a wide range of metals. Ligand **3** diastereoselectively chelates iron(II) to produce the corresponding mononuclear complexes in >99% diastereoselectivity. Hydrolysis of the ester linkages in the pure diastereomer of the deprotonated iron complex furnishes $\text{P-}(+)\text{-[Fe}(\text{HOCH}_2\text{PAPY})_2]$ with 85% enantioselectivity. This is the first inorganic asymmetric synthesis of a two-bladed propeller metal complex using classical organic methodology. (With A D Rae, R J Warr, A C Willis)

Tetrahedral Phosphine Cage Ligands and Complexes



Work is in progress concerning the metal-template synthesis of a tetrahedral phosphine cage complex by the route shown below. Molecular modelling and a crystal structure determination of $[\text{Cu}\{1,2\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2]\text{OTf}$ has established the chain length parameter for the alkylene groups. (With K Wells, A C Willis)

Quantum Chemical Design of Stereoregular Polyphosphines

Theoretical and synthetic work concerning the free-radical polymerisation of 1-phenylphosphetane and related compounds is underway. (With M L Coote, E H Krenske, J Steinbach)

