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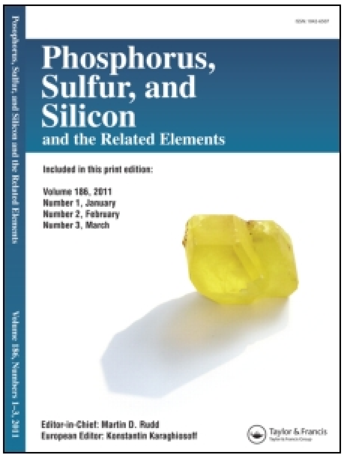

Phosphorus, Sulfur, and Silicon and the Related Elements

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Self-Assembly of Di- and Tri-Nuclear Metal Helicates Containing Homochiral Poly(Tertiary Phosphines) and Related Compounds

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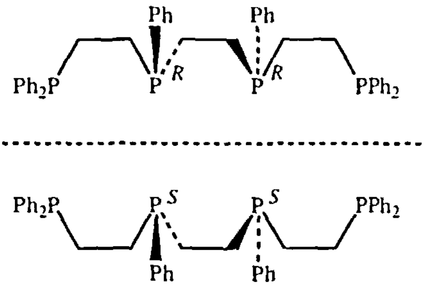
Appropriate enantiomerically pure poly(tertiary phosphines) in configurationally homogeneous form generate double-stranded double α-helix and side-by-side helix di- and tri-nuclear metal helicates with univalent copper, silver, and gold.

Keywords: enantiomerically pure poly(tertiary phosphines); dinuclear metal helicates

INTRODUCTION

A variety of suitably bridged dimers and oligomers of familiar chelating entities such as 2,2'-bypyridine, 1,10-phenanthroline, and related compounds, is now available for the self-assembly of double- and triple-stranded di-and oligo-nuclear metal helicates and other interesting structural motifs.[1] Moreover, the incorporation of a homochiral element in the helicating agent can lead to the highly stereoselective synthesis of a helicate.[2] Although suitable for the synthesis of helicates containing metal ions having *T*-4 or *OC*-6 coordination geometries, most imine-*N* containing helicating agents are unsuitable for the construction of double-stranded helicates from *SP*-4 metal ions such as palladium(II) and rhodium(I), which might have interesting properties in relation to the activation of small molecules, and catalysis. For this reason, and because of the paucity of data concerning phosphine–metal helicates, we have embarked on the synthesis of helicating poly(tertiary phosphines) and related compounds.[3]



(R^*,R^*)-(±)-tetraphos

Results and Discussion

The resolution of (R^*,R^*)-(±)-tetraphos[4] was achieved by the method of metal complexation with use of the readily prepared resolving agent (*R*,*R*)-2·CH_2Cl_2.[5] The pure enantiomers of the phosphine crystallise from acetone–ethanol as air-stable needles having mp 88 °C and $[\alpha]_D^{21}$ ± 20.5 (*c* 1, CH_2Cl_2).[3] Molecular mechanics calculations indicated that the binding of the individual enantiomers of the tetra(tertiary phosphine) with univalent silver and gold would produce energetically favoured double α-helical (a) or side-by-side (b) helical helicate conformers, rather than mononuclear metal complexes. Indeed, the structural determination of (–)-$[Ag_2\{(R,R)\text{-tetraphos}\}_2](PF_6)_2$ revealed one molecule each of the double α-helix and side-by-side helix conformers of the helicate in the cell; (–)-[Au_2{(*R*,*R*)-tetraphos}$_2$]($(PF_6)_2 \cdot CH_2Cl_2$, however, crystallised as the side-by-side helicate. The two helicates are related to each other by inversion of the central 10-membered ring containing the two metal ions, which has the chiral twist-boat–chair–boat (TBCB) conformation. Copper(I) forms a monomeric complex with the homochiral tetra(tertiary phosphine).[3] Because of the complexity of the $^{31}P\{^1H\}$ NMR spectra of the tetraphosphine helicates, the P_2As_2 ligand in which the terminal phosphorus atoms of tetraphos have been replaced by arsenic has also been synthesised, separated into diastereomers, and the racemic form resolved. The dicopper(I) complex of the resolved half-phosphine, which is a side-by-side helicate in the solid state, has a $^{31}P\{^1H\}$ NMR spectrum in acetonitrile-d_3 at 295 K that is consistent with an equilibrium mixture of mononuclear and dinuclear copper cations; the broad peak for the dicopper species is resolved at 228 K into three peaks corresponding to the double α-helix, side-by-side helix, and intermediate helicates. The crystalline silver(I) and gold(I) complexes of the P_2As_2 ligand are strictly isomorphous with the corresponding tetraphosphine helicates.

In other work, (*S*,*S*)-tetraphos has been converted in two high-yielding steps into the homologous hexa(tertiary phosphine), with retention of configuration of the two inner tertiary phosphine-*P* stereocentres, viz: (*S*,*S*,*S*,*S*)-, (*R*,*S*,*S*,*S*)-, (*R*,*S*,*S*,*R*)-hexaphos. The mixture can be quantitatively separated as the hexa-borane adducts by HPLC on a Waters μ-Porasil column. The three individual configurationally homogeneous helicating agents form double-stranded trinuclear metal helicates with univalent copper, silver, and gold, as evidenced by electrospray mass spectrommetry. The crystal and molecular structure of (–)-[Cu_3{(*R*,*S*,*S*,*R*)-hexaphos}$_2$]$(PF_6)_3 \cdot 3C_6H_6$ has been determined. The ORTEP plot of the cation of the salt is shown in Fig. 1. The structure is of a side-by-side helicate in which the two strands of the ligand are held together in a parallel arrangement by three copper ions. Each ligand in the cation completes two and one-half turns of a *M* helix. The side-by-side helical arrangements of the tetra- and hexa-tertiary phosphines about the metal ions are the structural motifs of the leucine repeat and zipper transcriptional proteins, wherein two polypeptide α-helices are held together in parallel side-by-side arrangements by hydrogen bonds.[6]

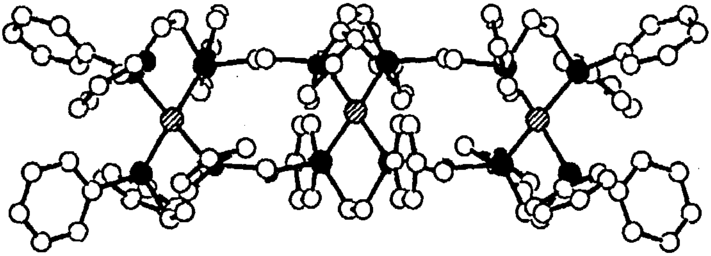


Fig. 1. ORTEP plot of cation of (–)-[Cu{(*R*,*S*,*S*,*R*)-hexaphos}$_2$](PF$_6$)$_3$·3C$_6$H$_6$

References

[1] J.-M. Lehn, *Supramolecular Chemistry* (VCH, Weinheim, 1995). C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* 97, 2005 (1997).

[2] W. Zarges, J. Hall, J.-M. Lehn, C. Bolm, *Helv. Chim. Acta* 74, 1843 (1991).

[3] A. L. Airey, G. F. Swiegers, A. C. Willis, S. B. Wild, *Inorg. Chem.* 36, 1588 (1997).

[4] R. B. King, P. N. Kapoor, *J. Am. Chem. Soc.* 93, 4158 (1971). J. M. Brown, L. R. Canning, *J. Organomet. Chem.* 267, 179 (1984).

[5] S. B. Wild, *Coord. Chem. Rev.* 166, 291 (1997).

[6] E. K. O'Shea, R. Rutkouski, P. S. Kim, *Science*, 243, 538 (1989).