Efficient asymmetry generation in the synthesis of oxo-rhenium(V) complex *cis*-[$ReOCl_2${$OCMe_2CMe_2OP(OCMe_2CMe_2O)$}py].

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Streszczenie

A simple procedure that randomly produces enantiomers of an oxo-rhenium(V) complex with a large enantiomeric excess (99 % *ee*) from optically inactive precursors is presented. The chirally autocatalytic synthesis is achieved by the spontaneous resolution of the conglomerate in a stirred crystallization following the formation of the complex in the reaction system. The results are supported by circular dichroism spectroscopy. One of the most intriguing challenges of stereochemistry is deracemization and the preparation of homochiral compounds.[1] Despite the great progress in asymmetric organic synthesis, there are only several instances of genuine “absolute” asymmetric preparation of inorganic compounds,[2] these include spontaneous resolution processes too.[3] Thus, a partial photoresolution either in circularly polarized light[4a,4b] or a parallel magnetic field[4c] has been observed for the $[Cr(ox)_3]^{3-}$ ion and its derivatives. Gillard and his associates have described the synthesis of the chiral polysulphide $(NH_4)_2[Pt(S_5)(S_6)_2]\cdot 2\,H_2O$.[5] The complex crystallizes spontaneously with one enantiomer in excess. It was obtained from a well-stirred water reaction mixture of K_2PtCl_6 and an excess of $(NH_4)_2S_n$, maintained at pH 9.4. Kondepudi and co-workers have shown that, whereas the crystallization of $NaClO_3$ from unstirred solutions yields a racemic conglomerate of (+)- and (−)-$NaClO_3$ (cubic space group $P2_13$), vigorous stirring triggers spontaneous symmetry breaking and produces almost exclusively crystals of single handedness.[6] Asakura et al. have demonstrated the generation of optically active *cis*-$[CoBr(NH_3)(en)_2]Br_2$ (en=1,2-ethanediamine) from optically inactive substrates in a stirred suspension by a chiral autocatalysis mechanism.[7] More recently, it has been reported that the crystallization of $NaClO_3$ from a solution irradiated by antiparallel-spin electrons results in dextrorotatory crystals in excess, whereas irradiation by parallel-spin positrons yields

crystals with the opposite handedness.[8] Keszthelyi and Szabó-Nagy have described a small enantiomeric excess found in polycrystalline material upon crystallization from racemic solutions of (+)- and (−)-tartrate(2−) with either (+)- and (−)-$[Co(en)_3]^{3+}$ or $[Ir(en)_3]^{3+}$ ions.[9] The authors of the latter two works have claimed that the observed partial deracemization is because of electroweak forces. Clearly, these preparations could only be successful under nonequilibrium conditions involving physical fields and/or autocatalytic chirality-amplification mechanisms. Nevertheless, in the preparation of transition-metal complexes, the generation of chiral asymmetry with substantial optical yields still remains rather rare.