Title (en)

NOVEL P-CHIRAL FUNCTIONALISED ARYLPHOSPHINES AND DERIVATIVES, THE PREPARATION AND USE THEREOF FOR ASYMMETRICAL CATALYSIS

Title (de)

NEUE P-CHIRALE FUNKTIONALISIERTE ARYLPHOSPHINE UND DERIVATE, IHRE HERSTELLUNG UND IHRE VERWENDUNG ZUR ASYMMETRISCHEN KATALYSE

Title (fr)

NOUVELLES ARYLPHOSPHINES P-CHIRALES ORTHO-FONCTIONNALISEES ET DERIVES: LEUR PREPARATION ET UTILISATION EN CATALYSE ASYMETRIQUE

Publication

EP 1899358 A2 20080319 (FR)

Application

EP 06778624 A 20060620

Priority

- FR 2006001394 W 20060620
- FR 0506226 A 20050620

Abstract (en)

[origin: FR2887253A1] Optically active organo phosphorus compound (I) in which the phosphorus atom carries chirality and a (hetero)aryl group functionalized in position ortho or 2, is new. Optically active organo phosphorus compound of formula (I) in which the phosphorus atom carries chirality and a (hetero)aryl group functionalized in position ortho or 2, is new. P 1>asymmetric P; m : >=1; n : 0-1; E : 2 electrons, BH 3, HBF 4, TfDH, HClO 4, HPF 6, HBr, HI, HCl, HF, CH 3COOH, CH 3COOH or MsOH; R 3>, R 4>H, 1-4C alkyl or 1-4C alkoxy (optionally substituted by F and/or 1-4C alkyl or 1-4C alkoxy (optionally substituted)); R 3>R 4>5-6C cycloalkane, dioxolane, dioxane or Ar e.g. naphth-1,8-diyl (optionally substituted); z : bond between (CR 3>R 4>) nand Z; Ar 1>4-14C (poly)aromatic ring (bonded to P 1>by a bond (x) and bonded to a group Z(CR 3>R 4>) nby a bond (y), where Z(CR 3>R 4>) nis in ortho or 2 position to P 1>) (optionally includes N, O, S or optionally carry N, O, Si, halo and/or optionally substituted 1-10C alkyl and/or alkoxy or form a cyclic ring of Ar and P as phosphino-Ar e.g. phosphinobenzene, 1-phosphinonaphtalene, 2-phosphinonaphtalene, N(R 5>)-2-methyl-7-phosphinoindole or N-(R 5>)-7-phosphinoindoline and Z(CR 3>R 4>) n-Ar-phosphino is N-(R 5>)-2-phosphinopyrrole or N(R 5>)-2-phosphmoindole); R 5>e.g. a carbon skeleton of formula (II); OR 5>(when m is 1) : e.g. 2,3- dihydro-2,2-dimethyl-7-benzofuranyl ring of formula (III); Z : OR 5>, SR 5>, SO 2R 5>, N(R 6>R 7>), C(O)N(R 6>R 7>), N(R 5>), 1-10C trialkylsilyl, triphenylsilyl, 5-14C (hetero)aryl (optionally substituted by F or 1-10C alkyl); A : C, O, S or TsN, CH, CH 2, Si(R 51>) 2-O-Si(R 51>) m1, benzene or pyridine; R 51>1-10C alkyl; m1 : >=1; A 1>-A 4>CH 2or (R 51>)CH; B 1>-B 4>CH 2, C(O), SO 2, (R 8>R 9>)Si, C(O)N or C(O)O; R 8>, R 9>1-18C alkyl, 5-8C cycloalkyl or 6-10C aryl (all substituted by alkyl, alkenyl or aryl, containing heteroatoms of O, N, Si, P or halo); k1-k4 : 0-10; l1-l4 : 0-1; x1-x4 : bonds between A and A 1>-A 4>; y1-y4 : bonds between A 1>-A 4>and B 1>-B 4>respectively; z1-z4 : bonds between B 1>-B 4>and O, S, N or NC(O) terminals; P 01>asymmetrical phosphorus atom with P 1>(where P 01>has absolute configuration); E 01>E; Q 1>C(Me) 2or Si(Me) 2; R 52>H, 1-10C alkyl e.g. methyl or tert-butyl; and either R 1>H, Cl, Br, I or F, 1-18C alkyl, 5-7C cycloalkyl, 4-14C (hetero)aryl (optionally substituted by alkyl, alkoxy or aryl and/or by heteroatoms e.g. O, N, Si, P, halo), 5-14C aryloxy, 1-18C alkoxy (optionally having C or substituted halo, nitrogenized groups of 4-6C aliphatic, 1-18C (di)alkylamino (where the alkyl have asymmetrical carbon atoms C and possibly substituted by heteroatoms) or Z(CR 3>R 4>) n-Ar); R 2>e.g. 1-18C alkyl, 5-7C cycloalkyl, 4-14C (hetero)aryl (optionally substituted by alkyl, alkoxy or aryl and/or by heteroatoms e.g. O, N, Si, P, halo), vinyl or alkoxy; or R 1>R 2>2-3C hydrocarbonated aminoalkoxy (containing asymmetrical carbon atoms C*). Full Definitions are given in the DEFINITIONS (Full Definitions) Field. Independent claims are included for: (1) the preparation of (I) using optically active oxazaphosphacycloalcane-borane of formula (Ib) derived from a optically active aminoalcohol of formula (HN(R 6>)-Q 2>-OH); (2) phosphine-metal complexes of formula M pL q(X 1>) r(S v) s(S 1>v) s1H tto carry out asymmetrical syntheses in organic chemistry, comprising a transition metal and at least optically active form of (I) as ligand; and (3) preparation of the phosphine-metal complexes comprising reacting the transition metal donor with (I) in the presence of a solvent. M : rhodium, ruthenium, iridium, cobalt, palladium, platinum, nickel or copper; L : optically active compound (I); S v, S 1>vH 2O, MeOH, EtOH, amine, 1,2-diamine (optionally chiral), pyridine, ketone e.g. acetone, ether e.g. THF, sulfoxide e.g. dimethyl sulfoxide, amide e.g. dimethyl formamide or N-methylpyrrolidinone, olefin e.g. ethylene, 1,3-butadiene, cyclohexadiene, 1,5-cyclo-octadiene, 2,5-norbornadiene, 1,3,5-cyclooctatriene, nitrile e.g. acetonitrile, benzonitrile, 5-12C arene or eta- aryl (optionally substituted by 1-5C alkyl, iso- or tert-alkyl, benzene, p-cymene, hexamethylbenzene or pentamethylcyclopentadienyl); p : 1-2; q : 1-4; r : 0-4; s, s1, t : 0-2; R 10>methyl, (trimethylsilyl)methyl, isopropyl, tert-butyl, adamantyl, 5-7C cycloalkyl, 4-14C aryl (optionally substituted) or ortho-Z(CR 03>R 04>) n-Ar; n : 0-1; Q 21>2-3C alkyl (having asymmetrical carbon, and bonded to N by R 06>containing a cycle); and Ar : phenyl or naphthyl (optionally substituted 1-10C alkyl and/or alkoxy (both optionally substituted or form a cycle)). Provided that when the complex cationic then X 1>is anionic ligand coordinant e.g. Cl, Br or I, anion groups e.g. OTf, BF 4, ClO 4, PF 06, SbF 6, BPh 4, B (C 6F 5) 4, B(3,5-di-CF 3-C 6H 3) 4, p-TsO, OAc or CF 3CO 2, pi -allyl, 2-methyl allyl. When the complex is anionic then X 1>is cation e.g. Li, Na, K or ammonium (optionally substituted by alkyl). [Image] [Image] [Image] [Image].

IPC 8 full level

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CPC (source: EP US)

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