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Article - 2013, Vol.42, No.1

37-39

Synthesis of Chiral Bis-MOP-type Diphosphines. Chelating Effect in Nickel-catalyzed Phosphination

Artur R. Abreu ^{1, 2}, Andreia F. Peixoto ¹, Ana R. Almeida ¹, Mirtha A. O. Lourenço ¹, Ângela C. B. Neves ¹, J. Carles Bayón ², Mariette M. Pereira ¹

https://doi.org/10.1246/cl.2013.37

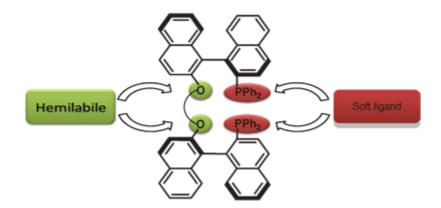
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Chiral bis-MOP-type diphosphines with alkyl and pyridyl bridges connecting the two binaphthyl units have been synthesized via [NiCl₂(dppe)]-assisted phosphination of the corresponding aryl triflates. The effect of the amount of the nickel complex on the reaction yield was investigated. Catalytic and even stoichiometric amounts of the complex proved to be insufficient to promote an efficient phosphination, but the use of an excess of the metal complex provides good yields.

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Chelate Size Dependence of Dihydrogen-Hydride Exchange in Ruthenium(II) Molecular Hydrogen Complexes with Diphosphines [RuH(η 2-H2)(P-P)2]PF6 (P-P = Ph2P(CH2)nPPh2; n = 2,3,4)

Masahiko Saburi, Ko Aoyagi, Tamotsu Takahashi, Yasuzo Uchida

The introduction of H_2 gas into CD_2CI_2 solutions of the five-coordinate complexes [RuH(P-P)₂]PF₆ (1) resulted in the spontaneous generation of molecular hydrogen complexes [RuH(η^2 -H₂)(P-P)₂]PF₆ (2) (P-P = 1,3-bis(diphenylphosphino)propane, 1,4-bis(diphenylphosphino)butane). ¹H-NMR measurements revealed that the dihydrogen-hydride exchange for a series of complexes 2 depends significantly on the size of diphosphine chelate.

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bcsj 1984 - Vol.57 , No.12, pp. 3595 - 3596

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The Phosphorus-31 Nuclear Magnetic Resonance Spectra of Bis(acetylacetonato)cobalt(III) Complexes Containing Bidentate Diphosphines Yoshio Koike, Toshio Takayama, Masatoshi Watabe

The phosphorus-31 nuclear magnetic resonance spectra of [Co(acac)₂(P-P)]⁺(P-P=diphosphine ligand) of the Werner type were measured, and the coordination chemical shifts were compared with those of complexes studied before. The coordination chemical shifts of the five-membered chelate ring were twice as much as those of the six-membered ring.

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cl 1989 - Vol.18 , No.2, pp. 263 - 266

Novel Synthetic Method of Phenol from Benzene Catalysed by Perfluorinated Hemin Shinji Tsuchiya, Manabu Seno

New perfluorinated hemin carrys out hydroxylation of benzene by hydrogen peroxide at room temperature and an atmospheric pressure. The turnover for phenol produced for 2 hours is 55. This hemin also catalyses the epoxidation of cyclooctene by hydrogen peroxide.

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cl 1996 - Vol.25 , No.11, pp. 1007 - 1008

New Chiral Diphosphines, 2,3-Bis(siloxy)-1,4-bis(diphenylphosphino)butanes, and Their Cationic Rh(I) Complexes: Synthesis and Structures

Kohei Tamao, Kazunori Nakamura, Shigehiro Yamaguchi, Motoo Shiro, Seiki Saito

A series of 2,3-bis(siloxy)-1,4-bis(diphenylphosphino) butanes SILOPs, possessing various siloxy groups, and their Rh(I) complexes have been prepared. The X-ray structure of a SILOP shows a staggered conformation with two siloxy groups in the anti positions. The X-ray crystal structure of a cationic Rh(I)-SILOP complex, however, shows an *anti* arrangement of not the two siloxy groups but the two silyl groups with respect to the O–O axis, which reinforces the C_2 -symmetrical environment around the metal center.

[Full Text PDF]

cl 2010 - Vol.39 , No.7, pp. 758 - 759

Synthesis, Structure, and Reversible Deprotonation of a Half-sandwich Iridium Complex Bearing a Chelating Oxime Ligand

Megumi Watanabe, Yohei Kashiwame, Shigeki Kuwata, Takao Ikariya

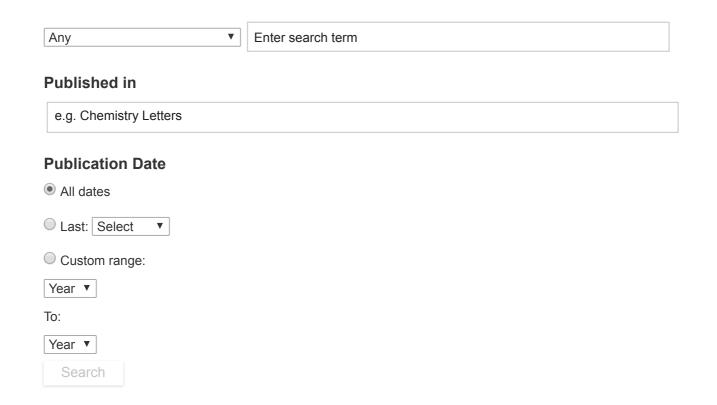
A reaction of [{Cp*IrCl(μ -Cl)}₂] (Cp* = η^5 -C₅(CH₃)₅) with 1-(pyridin-2-yl)ethanone oxime (PyNOH) afforded the cationic oxime complex [Cp*IrCl(PyNOH)]Cl (3) with an acidic OH group at the β -position to the metal center. Complex 3 underwent reversible deprotonation to give the corresponding oximato complex [Cp*IrCl(PyNO)] (4), while treatment of 3 with silver triflate in acetonitrile led to the formation of the dicationic complex [Cp*Ir(PyNOH) (CH₃CN)][OTf]₂ (5, OTf = OSO₂CF₃). The detailed structures of 3–5 have been determined by X-ray crystallography.

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