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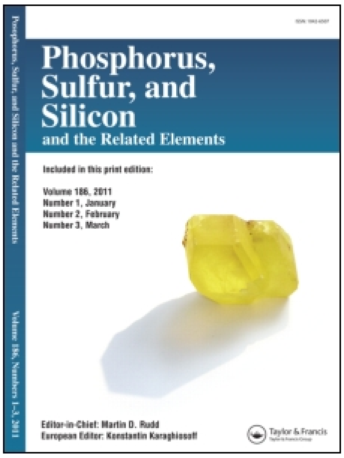

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Asymmetric Synthesis of Phosphinous Tungsten Complexes

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Asymmetric Synthesis of Phosphinous Tungsten Complexes

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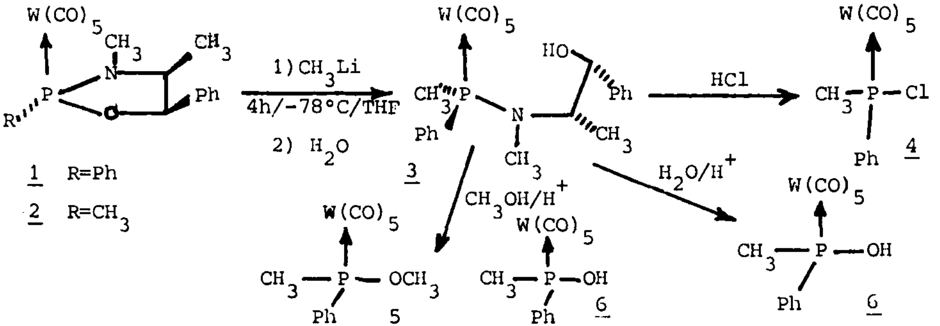

The asymmetric synthesis of phosphinous compounds from diheterophosphacycloalkane-1,3,2 was investigated in a transition metal complex series. Complexes 1 and 2 were prepared from diaminophosphine, (-)-ephedrine and W (CO)$_5$ THF (1: δ^{31}P=+147,6 ppm ; J_{PW}=313 Hz $M^{\cdot+}$=595 ; 2 δ^{3}P=+156 ppm J_{PW}=304 Hz $M^{\cdot+}$=533 ; 90%dp) in two steps. Methyl lithium reacted with 1 to give stereospecific 3 (80%Yield) by P-O linkage (3 δ^{31}P=+64 ppm ; J_{PW}=261 Hz ; $M^{\cdot+}$-28=583). The aminophosphine complex 3 was stereochemically stable and was used for studies of synthetic applications. HCL gas reacted with 3 in CH_2Cl_2 to give the non optically active chlorophosphine complex 4 (δ^{31}P=+103,6 ppm ; J_{PW}=290 Hz ; $M^{\cdot+}$=482). This compound immediately gave salt 6 (δ^{31}P=+66,7 ppm ; J_{PW}=240 Hz) by reaction with (-)-menthol and triethylamine. The acid methanolysis of 3 gave a mixture of 5 and 6 and the unchanged (-)-ephedrine salt [5:30% yield ; δ^{31}P=+114 ppm ; J_{PW}=280 Hz ; $[\alpha]_D$=+1,2° (CH_2Cl_2) ; $M^{\cdot+}$=478 ; 6 : 60% yield ; δ^{31}P=+102,9 ppm ; J_{PW}=264 Hz ; $[\alpha]_D$=+16,9° (CH_2Cl_2) ; $M^{\cdot+}$=464].Compound 6 was thus obtained with a 80% yield and a specific rotation of + 20,2° (CH_2Cl_2) in isopropanol/H_2SO_4 5M medium. The enantiomeric excess of 6 was determined by RMN^{31}P. Acid hydrolysis of 3 or the reaction with CH_3SO_3H, gave phosphinous acid complex 6 with an optical rotation of + 4,8° or-1,8° respectively. These results provide precious informations about the stereochemistry and reactivity of the P-N linkage in this aminophosphine transition metal series, which differs notably from that of the corresponding (PO) N bond.