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New Chiral Ligands and Complexes from α-Amino Acids

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N-diphenylphosphinoamino methyl/ethyl esters, dppam, react with [PtCl₂(cod)] and [RhCl(cod)]₂ to give cis-[PtCl₂(dppam-P)₂] and [RhCl(cod)(dppam-P], while interaction of dppam with [PdCl₂(cod)] leads to different complexes.

Keywords: N-diphenylphosphinoamino esters; [PtCl2(cod)]; [RhCl(cod)]2; [PdCl2(cod)]

INTRODUCTION

Chiral Complexes are very important in catalytic asymmetric synthesis. As natural and readily available chiral compounds, amino acids are often employed as starting material for chiral ligands. There are several reports which involve N,N-bis(diphenylphosphino)amino esters, but no N-mono(diphenylphosphino)amino ester complexes are found except one report about the stereoselective synthesis of the N-phosphorus(V) substituted amino acids via the N-phosphorus(III) derivative of amino acids. Here we present some new N-diphenylphosphinoamino esters and the corresponding chiral complexes of these ligands.

RESULTS AND DISCUSSION

S-α-amino esters react with one equivalent of chlorodiphenylphosphine to give S-N-diphenylphosphinoamino esters 1 in the presence of triethylamine in yields up to 90% (SCHEME 1).

SCHEME 1

Compounds 1 react with [PtCl₂(cod)] and [RhCl(cod)]₂ to give cis-[PtCl₂(dppam-P)₂] 2, [RhCl(cod)(dppam-P)] 3 as expected (SCHEME 2 and SCHEME 3).

SCHEME 2

SCHEME 3

It is surprising that 1 and [PdCl₂(cod)] lead to different products. As shown by SCHEME 4, 1a and 1c coordinate with [PdCl₂(cod)] to give the surprising chloro-bridged binuclear complexes 4. But 1e and [PdCl₂(cod)] gave a chelate hemilabile complex cis-[PdCl₂(dppme-P,S)] 5 (SCHEME 5). Other ligands react with [PdCl₂(cod)] to result in rather complicated mixtures which are difficult to separate.

4a $R = CH_3$, $R' = CH_3$ 4c $R = CH(CH_3)_2$, $R' = CH_3$ SCHEME 4

SCHEME 5

Complexes 2a, 4a, and 5 have been confirmed by X-ray crystallographic analysis.

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