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Synthesis of stibine $SbPhR^1R^2$ and their use as ligand in the amidocarbonylation of alkenes with $Co_2(CO)_8$ as precursor

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Abstract

Treatment of bis(1-phenylethynyl)-phenylstibine with 2,4,6-trimethyl magnesium bromide promotes the nucleophilic displacement of one ethynyl group, as was previously reported by Kurita, affording the phenyl (1-phenylethynyl)mesitylstibine. This antimony compound was used as a ligand in order to modify the $Co_2(CO)_8$ catalytic system for the amidocarbonylation (Wakamatsu reaction) of cyclohexene, cyclopentene, 1-hexene, and 1-pentene. This new modified catalytic system is capable of affording moderate yields of *N*-acetyl-α-aminoacids.

Keywords: Antimony; Stibine ligands; Amidocarbonylation; Wakamatsu reaction; Homogeneous catalysis

1. Introduction

The preparation of organometallic compounds of some elements of the group 15 involves the nucleophilic displacement of the halogen group on appropriate metal halides (MR_3, M = P, As, Sb, Bi) [1]. However, this method has been proved to be unsatisfactory for the preparation of unsymmetrical compounds, all the halogen atoms are replaced simultaneously because the halogen moieties are highly reactive as leaving groups and also organomagnesium and organolithium reagents have high nucleophilicity. Only a few limited examples have been reported regarding success in the preparation of asymmetric stibines.

The alkene amidocarbonylation reaction (Wakamatsu's reaction) [2] constitutes an excellent method to introducing two carbonyl groups in a one pot process, starting with olefins as substrates. This reaction has been used in obtaining *N*-acyl aminoacids, which have a wide range of applications.

We have previously reported results obtained in the synthesis of *N*-acyl aminoacids, using triarylstibines and triarylphosphines as ligands in a homogenous-phase system with cobalt as a catalytic precursor in the amidocarbonylation process [3]. The effect of the phosphines was compared to that of the stibinic ligands, and the study showed that the latter have better yields and are more selective to the linear amino acids than that presented by the phosphine ligands.

Forbus and Brown [4] reported the effect of the steric requirements, as well as the basicity of different phosphines in octacarbonyldicobalt substitution reactions. These study demonstrated that the rate-limiting step in the process is the dissociation of carbon monoxide from the $Co_2(CO)_8$. Furthermore, Wendt and Elding [5] carried out a comparative study of the *trans* influence and *trans* effect of triphenyl stibine and phosphines in transition metal complexes, and concluded that $SbPh_3$ has a greater trans effect than PPh_3. In that report, stibinic Pt (II) complexes reacted *ca*. 16 times faster than their phosphorous analogous.

This paper reports the use of a cobalt system modified with a PhR^1R^2Sb ligand, as a catalytic precursor in the amidocarbonylation reaction of some alkenes under mild operating conditions. To the best of our knowledge $R^1R^2R^3Sb$ compounds have not been previously used in the named process (Scheme 1).

2. Experimental

2.1. Synthesis of phenyl (1-phenylethynyl)mesitylstibine

2,4,6-Trimethylphenyl magnesiumbromide (5.5 mmol) at 0 °C was added (under nitrogen) to a stirred solution of 5 mmol

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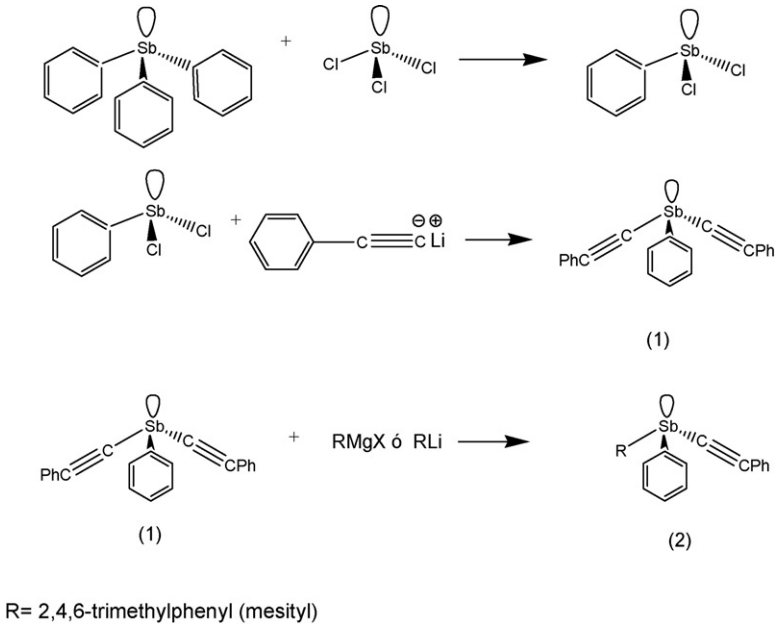


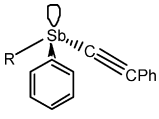
Scheme 1. Synthesis of phenyl (1-phenylethynyl)mesitylstibine.

of phenyldiethynylstibine (1) (which was prepared according to previous reports [6]) in dry ether (50 ml). The reaction mixture was stirred for 6 h, and then diluted with hexane and degassed water. The organic layer was washed with a solution of NaCl (10%) and dried over Na_2SO_4. After removal of the solvent in vacuo, the residue was eluted in a silica gel column chromatography (hexane 100%), affording a white solid (2) (73%), *m/z* (EI) 418(82)M^+, $\mu_{max/cm^{-1}}$, 2929 (–CH_3), 2135 (C≡C), RMN δ(500 MHz, $CDCl_3$) 2.53 (3H, s, Mesityl-Me) 2.68 (6H, s Mesityl-Me), 6.89 (1H, s, Mesityl-H, Ph, $J = 1$ Hz), 6.897 (1H, s, Mesityl-H, Ph, $J = 1$Hz), 7.29–7.35 (6H, m, Ph-H, $J = 3.5$ Hz), 7.47 (2H, dd, Mesityl-Ph-H, $J = 6.9$ Hz), 7.6 (2H, dd, Ph-H, $J = 7.5$ Hz).

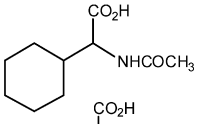
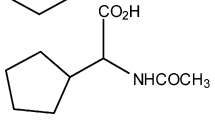
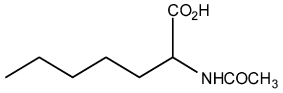
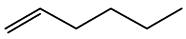
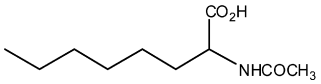
2.2. General catalytic procedure

A solution of 3.46 mmol of the alkene, 5.20 mmol acetamide, 0.12 mmol of $Co_2(CO)_8$ and 0.12 mmol of PhR^1R^2Sb, in 10 ml of dry THF (in a Schlenk tube), was transferred to a stainless steel reactor (PARR) under nitrogen. Then, the reaction was taken to the desired pressure (28 bar, CO/H_2, 3/1), and warmed in an oil bath, at 120 °C for 20 h. At the end of this period, the reactor was cooled and the gases liberated. The solution was worked up in order to obtain the reaction products [3]. The named solution was also analyzed by GC and GC–MS in order to quantify the remaining substrate and the by-products of the reaction (aldehydes and alcohols).

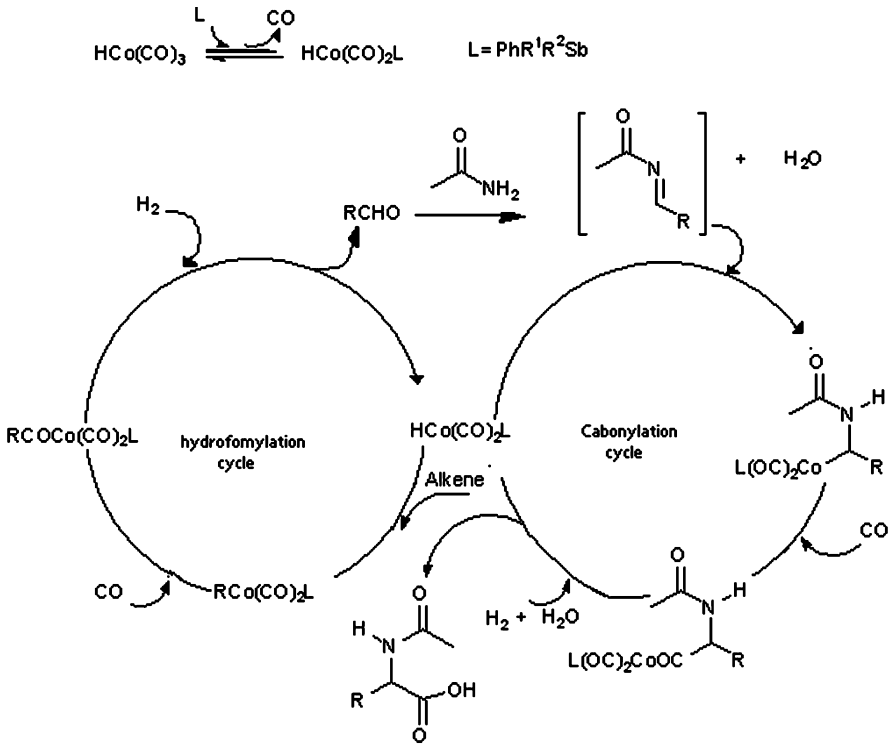
Table 1
N-Acetylaminoacids via co-stibine catalysed amidocarbonylation



\+ Alkene → ($Co_2(CO)_8$, CO/H_2) N-Acetylaminoacid

Alkene	N-Acetylaminoacid	Yield %	Branched Yield %
		73	-
		64	-
		52	17
		41	20

$T = 120$ °C, $t = 20$ h; $Co_2(CO)_8$/Sb(phenyl)(1−phenylethynyl)mesityl (1:1) 0.12 mmol:acetamide 5.20 mmol (1.5 equiv.), alkene 3.46 mmol (1 equiv.); syn−gas pressure CO/H_2 (3:1) (28 bar); THF 10 ml.



Scheme 2. Mechanism of amidocarbonylation reaction PhR^1R^2Sb/Co system.

3. Results and discussion

Previous reports using R_3Sb organoantimony compounds as ligands in a modified cobalt system for the hydroformylation and amidocarbonylation reactions of alkenes [3,7–9], confirmed the importance of the stibines as ligands in the aforementioned homogeneous catalytic process. We found that this modified catalytic system not only increases the activity, but also improves the selectivity of the reaction to the linear products in very good proportion, compared to the behaviour of phosphines ligands [7].

Based on the foregoing results, we carried out some experiments using compound 2 as ligand in the aforementioned modified cobalt precursor, with the aim of proving its efficiency. The results are shown in Table 1. As may be observed, this catalytic system promotes the reaction.

In Scheme 2, a possible reaction pathway of amidocarbonylation is suggested as sequence of hydroformylation cycle, imide formation and a carbonylation cycle. Studies regarding the influence of $R^1R^2R^3Sb$ ligands on possible stereocontrol in Wakamatsu's reaction are in progress.

Acknowledgments

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