Heterobimetallic complexes containing iron (II) and hexa-coordinated organosilicon

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Abstract: Heterobimetallic complexes of the type R₂Si(HL)Cl₂ and R₂SiL₂ (where R = Me, Et, Ph; L = ferrocenyl arylhydrazone) have been synthesized at 40 °C to 50 °C and at room temperature (25 °C), respectively, and characterized by elemental analysis, molar conductance, infrared and NMR (¹H, ¹³C and ²⁹Si) spectral data. The ligands behave as bidentate, coordinating through the azomethine nitrogen and the oxygen in the amidic and the imidic acid forms of the ligand at low temperature and at room temperature, respectively. The ligands and their organosilicon complexes have been evaluated for the antifungal activity against Alternaria alternata, Fusarium oxysporum and Rhizoctonia solani, as well as antibacterial activity against gram negative, Escherichia coli and gram positive, Bacillus subtilis, at 28 °C. Organosilicon complexes of ferrocenyl arylhydrazone were found to be more potent than the parent ligands.

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1 Introduction

Hydrazones are known to possess wide variety of biological activities [1–3] and inhibit many enzymatic reactions in cell. The incorporation of various substituents onto the hydrazones have a marked effect on their biological activity. The activity of some biologically active hydrazones was appreciably enhanced on coordination with metal ion or with organosilicon halides [4–6]. The ferrocenyl unit was claimed to be a useful moiety in the synthesis of new biologically active compounds [7, 8]. If a ferrocenyl unit is incorporated into the organic moiety it often shows unexpected biological activity, as in the new ferrocene-chloroquine analogue [9] and ferrocenic artemisinin derivative [10].

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The replacement of an aryl group with a ferrocenyl moiety improves antibiotic activity in the penicillins and cephalosporines. Moreover, it is chemically stable, less toxic than the aryl counterpart and is able to cross the cell membrane [11]. Therefore, we have synthesized heterobimetallic complexes by reacting ferrocenyl aroylhydrazones with dichlorodiorganosilane, and studied the effect of coordination on antimicrobial activity to explore their use as potential biocidal agents.

2 Experimental

All operations were carried out under dry nitrogen atmosphere. The solvents used were dried by conventional methods. \( \text{R}_2\text{SiCl}_2 \) (\( \text{R} = \text{Me, Et and Ph} \)) and \( \text{Cp}_2\text{Fe} \) were obtained through Aldrich and used without further purification. The ligands and all the dichlorodiorganosilane complexes were analyzed for C, H, N using an automatic elemental analyzer, model 1600. \(^1\text{H} \) NMR spectra of the ligands and their complexes were recorded on 390 (90 MHz) spectrometer, in CDCl\(_3\) and two drops of DMSO-\( \text{d}_6 \) using TMS as an internal standard. The \(^{13}\text{C} \) NMR spectra of the compounds were obtained in a saturated CDCl\(_3\) solution (77.0 ppm) along with \(^{29}\text{Si} \) NMR on a 22.49 MHz JEOL FX600 spectrophotometer using TMS as an internal standard. Infrared spectra were recorded, as KBr pellets, using a Biorad FTS-7 infrared spectrophotometer. Molecular weights of the complexes were determined by cryoscopic method in dry nitrobenzene. Low temperatures were maintained using cryo-cool model CC-100 II, Neslab, Italy. The ligands (HL) were prepared in two steps: (i) by synthesizing substituted benzoic acid hydrazide; (ii) by synthesizing substituted ferrocenyl aroylhydrazone as reported in the literature [12].

2.1 Reaction of (HL) with \( \text{R}_2\text{SiCl}_2 \) at 25 °C

To a solution of ferrocenyl aroylhydrazone (20 mmol) in 40 mL of dry petroleum ether (40 - 60 °C), was added with constant stirring a solution of dichlorodiorganosilane (10 mmol) in the same solvent. This reaction is carried out while flushing nitrogen gas continously in order to evaluate HCl gas so formed. The reaction mixture was stirred for 1 hour at room temperature. The violet colored complexes (yield 60-70%) obtained were filtered, washed with dry petroleum ether (40-60 °C) and dried under vacuum.

2.2 Reaction of (HL) with \( \text{R}_2\text{SiCl}_2 \) at -40 °C to -50 °C

Ferrocenyl aroylhydrazone (10 mmol) was dissolved in 30 mL of petroleum ether and cooled to approximately -40 °C to -50 °C. To this solution, the required amount of dichlorodiorganosilane (10 mmol), in petroleum ether, was cooled to -40 °C and added dropwise with constant stirring under a dry nitrogen atmosphere. The reaction mixture was stirred for 2 hours at low temperature. The dark colored silane complexes (yield 60-70%) obtained were filtered, washed with dry petroleum ether and dried under vacuum.