Silsesquioxane Chemistry. 12 [1]

Preparation and Complexation of a Novel Silsesquioxanyl Phosphine Ligand

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Received September 16th, 2002.

Abstract. The reaction of the monofunctional closo-silsesquioxane silanol derivative Cy7Si8O12OH (3, Cy = c-C5H11) with tris(dimethylamino)phosphine afforded the novel silsesquioxanyl phosphine ligand Cy7Si8O12OP(NMe2)2 (4) in virtually quantitative yield. The complexes [Cy7Si8O12OP(NMe2)2]2PtCl2 (5) and [Cy7Si8O12OP(NMe2)2]2Mo(CO)4 (6) were obtained in excellent yields upon treatment of 4 with (COD)PtCl2 (COD = 1,5-cyclooctadiene) and (NBD)Mo(CO)4 (NBD = norbornadiene), respectively. An attempted preparation of the bis(silsesquioxanyl)phosphine (Cy7Si8O12O)2P(NMe2) led to the formation of the known disiloxane derivative (Cy7Si8O12)2O (7), instead.

Keywords: Silsesquioxanes; Silsesquioxanyl phosphine ligand; Platinum; Molybdenum

Silsesquioxan-Chemie. 12 [1]

Herstellung und Komplexierung eines neuen Silsesquioxanyl-Phosphin-Liganden

Inhaltsübersicht. Die Reaktion des monofunktionellen closo-Silsesquioxan-silanol-Derivats Cy7Si8O12OH (3, Cy = c-C5H11) mit Tris(dimethylamino)phosphan lieferte den neuartigen Silsesquioxanyl-phosphan-Liganden Cy7Si8O12OP(NMe2)2 (4) in praktisch quantitativer Ausbeute. Die Komplexe [Cy7Si8O12OP(NMe2)2]2PtCl2 (5) und [Cy7Si8O12OP(NMe2)2]2Mo(CO)4 (6) wurden in hervorragenden Ausbeuten durch Umsetzung von 4 mit (COD)PtCl2 (COD = 1,5-Cyclooctadien) bzw. (NBD)Mo(CO)4 (NBD = Norbornadien) erhalten. Ein Versuch, das Bis(silsesquioxanyl)phosphan (Cy7Si8O12O)2P(NMe2) herzustellen, führte lediglich zur Bildung des bekannten Disiloxanderivats (Cy7Si8O12)2O (7).

Introduction

Functionalized silsesquioxanes have been intensively investigated in the past decade for various reasons. They offer highly interesting possibilities as building blocks for silicious materials, catalyst model systems, homogeneous catalysts as well as novel polymer materials [2–11]. The most common silsesquioxane systems include the cube-octameric clusters (i.e. R8Si8O12) and incompletely condensed frameworks such as (c-C5H11)7Si7O8(OH)3 (1). Derivatization of 1 is the most promising synthetic pathway to functionalized silsesquioxanes, including metallalsesquioxanes and polymers bearing silsesquioxane units. For example, condensation of 1 with SiCl4 in the presence of triethylamine leads to clean formation of the chlorosilsesquioxane 2 (Scheme 1), which can easily be hydrolysed to give the hydroxysilsesquioxane 3 [12]. Metal-containing silsesquioxane derivatives of both 1 and 3 have been well investigated in view of their direct application as catalysts. However, much less is known about heteroatom-substituted silsesquioxane systems. Of special interest are phoshpine-functionalized silsesquioxane cages which would be ideal precursors for novel Si–O-anchored transition metal complexes. There are several examples of interesting polyfunctional phosphinodendrimers, based on polyhedral silsesquioxane cores bearing eight phosphinoalkyl functional moieties, in the literature [13–16]. However, virtually unknown are monofunctional phosphine ligands derived from silsesquioxane cage molecules. We report here the facile and straightforward synthesis of the novel ligand Cy7Si8O12OP(NMe2)2 (4, Cy = c-C6H11) as well as a first study of its complexation behavior towards transition metals (Pt, Mo).

Results and Discussion

As depicted in Scheme 1, the closo-silsesquioxan silanol derivative 3 is readily prepared by controlled hydrolysis of the chlorosilsesquioxane precursor 2 [12]. The room temperature reaction of 3 with tris(dimethylamino)phosphine, P(NMe2)3, in dichloromethane according to Scheme 2 afforded the novel silsesquioxane-substituted phosphine ligand Cy7Si8O12OP(NMe2)2 (4) in virtually quantitative
yield (Scheme 2). The reaction took place instantaneously after the addition of tris(dimethylamino)phosphate to a solution of the silanol 3. Compound 4 is directly obtained in an analytically pure state as only volatile dimethylamine is formed as a by-product in this reaction.

Scheme 2 Synthesis of silsesquioxanyl phosphine 4.

White crystalline 4 is sensitive to moisture and is readily soluble in organic solvents such as toluene, THF, and dichloromethane, and even in aliphatic hydrocarbons its solubility is quite high. Full characterization was readily achieved by spectroscopic methods and elemental analysis. An initial complexation study showed that the silsesquioxanyl phosphine derivative may be employed as a suitable ligand for transition metal complexes. In dichloromethane solution 4 reacted smoothly with (COD)PtCl2 (COD = 1,5-cyclooctadiene) to give the bis(ligand) complex 5 in nearly quantitative yield. A similar reaction of 4 with (NBD)Mo(CO)4 (NBD = norbornadiene) cleanly produced the molybdenum tetracarbonyl complex 6 also in high yield. Work-up of the reaction mixtures was simple and straightforward as the by-products 1,5-cyclooctadiene and norbornadiene, respectively, were readily removed together with the solvent in vacuo.

Scheme 3 Synthesis of metal complexes 5 and 6.

Both new complexes 5 and 6 were isolated as colorless, microcrystalline solids which are highly soluble in common organic solvents such as dichloromethane, chloroform, toluene, THF, diethyl ether, and hexane. They are thermally quite stable under inert atmosphere, but were found to decompose readily under the influence of moisture. Apparently suitable single crystals for X-ray diffraction studies could be grown from diethyl ether solutions upon cooling, but in all cases full refinement of the molecular structures was made impossible by severe disorder problems involving the cyclohexyl substituents of the silsesquioxane cages.

Full characterization of all new compounds was achieved by spectroscopic methods and elemental analysis. In the 1H NMR spectra compounds 4 – 6 show characteristic multiplets at 1.75 ppm, 1.25 ppm and 0.75 ppm for the cyclohexyl groups (C6H11). The PNC3H groups display a characteristic doublet at 2.55 ppm with 3J(HP) = 9.78 – 10.50 Hz. In the 31P{H} NMR spectrum 4 shows one sharp singlet at 127.05 ppm in the expected area [17]. Both 5 and 6 display sharp singlets in the 31P{H} NMR spectra at 60.65 ppm and 153.61 ppm, respectively. The low value of 1J(PPt) (2730 Hz) in 5 suggests that the two Cl ligands are arranged in the cis positions [17]. In the IR spectra all three compounds show strong broad bands at 1110 cm−1 attributable to the Si–O–Si vibration. Two strong ν(CO) bands in the spectrum of 6 indicate the presence of the cis isomer. In the CI-mass spectrum of 4 the molecular ion could be detected. Due to the large size of the molecules of 5 and 6 only fragments of the silanol ligands could be recorded in these cases using both CI−MS and FAB methods.

An attempt was made to synthesize the related bis(silsesquioxanyl) phosphine derivative (Cy2SiO11O)2P(NMe2). However, the reaction between equimolar amounts of 3 and
4 in dichloromethane solution at room temperature did not produce the desired product. Instead, only the known disiloxane derivative (Cy₇Si₈O₁₂)₂O (7) [18] besides (Me₂N)₂P(O)H [19] were formed as evidenced by the ³¹P NMR spectrum and mass spectrometric analysis (Scheme 4).

In summarizing these results, we have demonstrated that the reaction of silsesquioxane silanol 4 with tris(dimethylamino)phosphine provides a straightforward access to a novel silsesquioxanyl phosphine ligand, which is a useful precursor for the preparation of Si–O-anchored transition metal complexes.

**Experimental**

**General Comments:** All reactions were carried out in an inert atmosphere of nitrogen using standard dry box and Schlenk techniques [20]. IR spectra were recorded on a Perkin-Elmer FT-IR Spectrometer System 2000. NMR spectra were recorded at the Chemistry Department of the Otto-von-Guericke-Universität using a Leco CHNS 932 apparatus. Melting and decomposition points were determined on an Electrothermal IA 9100 apparatus. The starting materials 2 and 3 were synthesized according to literature procedures [12] and recrystallised from diethyl ether prior to use. Commercially available (Aldrich) P(NMe₂)₃ was used as received without any further purification.

**Scheme 4** Attempted preparation of (Cy₇Si₈O₁₂)₂P(NMe₂). 

[Cy₇Si₈O₁₂OP(NMe₂)₂]₂PtCl₂ (5): A solution of (COD)PtCl₂ (COD = cyclooctadiene) (37 mg, 0.1 mmol) in 5 ml of dichloromethane was added at room temperature in one portion to a solution of 4 (227 mg, 0.2 mmol) in 20 ml of dichloromethane. The reaction mixture was stirred for 2 h. After removal of the solvent in vacuo the product was obtained as a white microcrystalline solid in pure form. Yield 243 mg (0.96 mmol, 96%).

1H NMR (25 °C, CDCl₃): δ 5.25 (d, 3J(PH) = 9.78 Hz, 12H, P[CH(CH₃)₂]), 1.72 (br m, 35H, CH₂), 1.22 (br m, 35H, CH₂), 0.76 (br m, 7H, CH). ³¹P[H] NMR (25 °C, CDCl₃): δ 127.05 ppm (s). MS (CI–CH₄, relative intensity): m/z: 1014 (100 %), 955 (38 %), 871 (100 %). IR (KBr): 2918(s), 1115(vs).

[A Novel Silsesquioxanyl Phosphine Ligand](#)


