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Hydrosilylation cross-linking of silicon fluids by a novel class of iron(0) catalysts

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ABSTRACT

Iron(0) carbonyl complexes of the general formula $[Fe(CO)_3(L)]$, $[\{Fe(CO)_3\}_2L]$ stabilized by multivinylsilicon ligands (where L = diene, triene, tetraene, polyvinyl silicon derivatives) were examined as novel catalysts in the molecular model of cross-linking process as well as various polymeric silicone systems. In the model reactions between vinylheptamethyltrisiloxane and heptamethyltrisiloxane, these complexes proved to be efficient catalysts of dehydrogenative silylation, while in polymeric systems, made of silicone fluids such as poly(vinyl)siloxanes and polyhydrosiloxane, the hydrosilylation was efficiently catalyzed at elevated temperatures. The complexes examined when added to these silicon fluid mixtures proved to be still active after extended storage times, even when exposed to air and moisture. The NMR studies of stoichiometric reactions of $[Fe(CO)_3\{(H_2C{=}CHSiMe_2)_2O\}]$ with molecular substrates as well as the cross-linking catalytic tests in the liquid phase in the presence of these complexes allowed proposing a mechanistic scheme for the catalysis of hydrosilylation vs. dehydrogenative silylation, by the new iron carbonyl catalysts in which $[Fe(CO)_3]$ moiety is stabilized by multivinylsilicon derivatives.

1. Introduction

Multifunctional silicon hydrides and vinyl endblocked polydiorganosiloxanes are common components used for production of silicone elastomers cured via a hydrosilylation reaction [1].

Hexachloroplatinic acid and other soluble platinum complexes are commonly used as catalysts for this process. The platinum–alkenylsiloxane complexes, mainly the platinum(0)–vinylsiloxane complex (Karstedt's catalyst) and its derivatives are the most active and commercially used catalysts [2]. Therefore, in order to extend the storage time of silicone curing mixture, various inhibitors need to be added to the siloxane compositions containing the platinum catalyst to reduce or temporarily inhibit its catalytic activity [2].

We have recently published results on the synthesis and use of triorganophosphites [3–5] and tris(triorganosilyl)phosphites [6,7] as a new class of efficient inhibitors stabilizing the Pt(0)–Karstedt complex in siloxane compositions. The search for new and efficient hydrosilylation catalysts has brought about a synthesis of platinum complexes with dialkynyldisiloxane ligands, which proved to be very good catalysts for this process [8,9].

However, the possibility of replacing expensive platinum catalysts with catalytically active derivatives of cheaper transition metals such as Ru or Fe, is a promising alternative and a challenge for many research teams. Recently, Chirik, Ritter and Nakazawa groups have published results on the application of bis(imino)pyridine and terpyridine iron complexes in the hydrosilylation of alkenes by primary, secondary [10], and tertiary silanes [11–17] as well as dienes [18]. The iron triad (Fe, Ru and also Os) complexes, including their carbonyl complexes, competitively catalyze or photocatalyze hydrosilylation and dehydrogenative silylation [19,20]. The key step of this mechanism is the insertion of an olefin into M—H or M—Si bonds to give products of hydrosilylation and/or dehydrogenative silylation. An essential step of the two alternative reactions is actually the competitive β-H transfer from the two ligands (σ-alkyl and σ-silylalkyl) of the complex formed during the reaction (see Scheme 1).

We have recently developed a general strategy for the synthesis of new well-defined iron(0) carbonyl complexes $[Fe(CO)_3(L)]$ or $[\{Fe(CO)_3\}_2L]$ stabilized by multivinylsilicon ligands (where L = diene, triene, tetraene or polyvinyl silicon derivatives) (Scheme 2). Their structures were determined by spectroscopic and X-ray methods [21,22].

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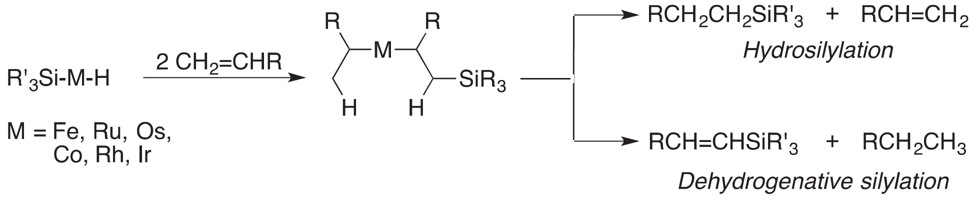


Scheme 1. Hydrosilylation vs. dehydrogenative silylation.

The aim of this paper is to report on the effectiveness of these complexes as new catalysts for silicone cross-linking as well as examine their catalytic activity in the reaction of heptamethylvinyltrisiloxane with heptamethylhydrotrisiloxane, as a molecular model for the silicone curing reaction.

2. Experimental

2.1. Methods and techniques

All manipulations were carried out under dry argon using standard Schlenk's and vacuum techniques. The chemicals were purchased from Aldrich and ABCR. Reagent grade pentane and benzene were distilled from sodium hydride under argon. Liquid state NMR spectra were recorded in toluene-d_8 using a Bruker Ultra Shield spectrometer (600 MHz) and referred to the residual protonated solvent peaks (^{1}H $\delta_H = 2.09$ ppm (−Me), ^{13}C $\delta_C = 20.05$ ppm (−Me) for toluene-d_8). The UV initiated reactions were performed using an UV light source LQ-400 (Gröbel UV-Elektronik GmbH), equipped with two liquid light guides (1 m long, diameter 8 mm) with lamp power of 400 W (irradiance: 1.5 mW/cm^2 (UV-A); 200 mW/cm^2 (UV-B), illuminance: 3.500 kLx, wave length: 280–600 nm). The mass spectra of the products were determined by GC-MS (Varian Saturn 2100 T equipped with a VF-5, 30 m capillary column). GC analyses were carried out on a Varian CP-3800 series gas chromatograph equipped with a VF-5, 30 m capillary column and TCD. Yield was calculated on the basis of $HSiMe(OSiMe_3)_2$ conversion, using the internal standard calculation method according to the formula $Y(\%) = S_a \cdot C_{HSi\equiv}$ (S = selectivity, C = conversion (%)) The progress of the curing process was monitored by differential scanning calorimetry (DSC) test method. DSC measurements were made using a Netzsch DSC200 apparatus. The instrument was calibrated with indium ($\Delta H = 28.4$ J/g). Analysis conditions (DSC): hold for 5.0 min at 30 °C, heat from 30 to 300 °C at 10 °C/min, under argon atmosphere.

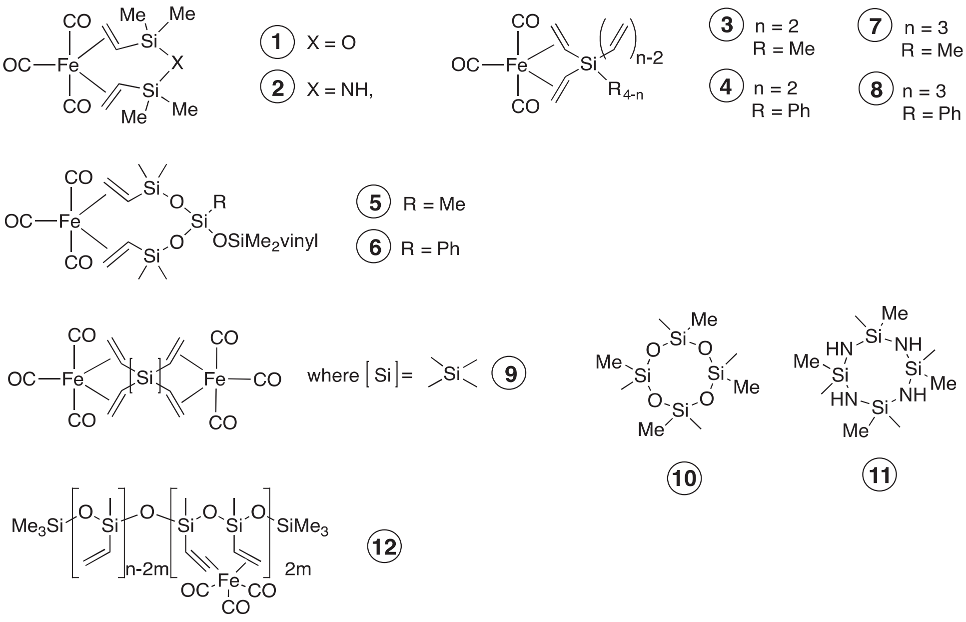
2.2. Preparation of vinyl-silicon stabilized iron(0) complexes

The iron(0) complexes of the type $[Fe(CO)_3(L)]$ or $[\{Fe(CO)_3\}_2L]$ (where L = diene, triene, tetraene, polyvinyl silicon derivatives), used for catalytic examinations were synthesized according to published method [21,22].

2.3. Catalytic examinations

2.3.1. General procedure for determination of iron(0) complexes catalytic activity in the molecular model reaction

The tests on the catalytic activity of iron(0) complexes in the model reaction were conducted in glass ampoules (or Schlenk tubes) filled with a mixture of vinylmethylbis(trimethylsiloxy)silane (1.593 mmol, 0.46 mL), heptamethylhydrotrisiloxane (0.796 mmol, 0.22 mL), toluene 1 mL and decane (5% of initial liquid substrates volume) as an internal standard, under argon atmosphere. The ampoules (or Schlenk tubes) were heated to a desired temperature in oil bath. The tests on the catalytic activity of iron(0) complexes in the model reaction, initiated by UV, were performed in glass ampoules (or Schlenk tubes) filled with a mixture of vinylmethylbis(trimethylsiloxy)silane (1.593 mmol, 0.46 mL), heptamethylhydrotrisiloxane (0.796 mmol, 0.22 mL) and decane (5% of initial liquid substrates volume) as an internal standard under argon atmosphere. The initial solutions were irradiated by UV light for 30 min at room temperature.



Scheme 2. Formulas of new iron complexes with multivinylsilicon ligands.