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Catalytic activity of iridium siloxide complexes in cross-linking of silicones by hydrosilylation☆

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Abstract

A series of catalytic examinations have shown that monomeric iridium siloxides ([Ir(cod)(PCy_3)($OSiMe_3$)] (**II**), [Ir(CO)$(PPh_3)_2$($OSiMe_3$)] (**III**) and [Ir(CO)$(PCy_3)_2$($OSiMe_3$)] (**IV**)) are effective catalysts for model homogeneous hydrosilylation of vinyltris(trimethylsiloxy)silane as well as cross-linking of commercial polysiloxane system. The results of stoichiometric reactions of iridium siloxide with heptamethyltrisiloxane and observed catalytic properties are consistent with the mechanism of catalysis involving a generation of the key-intermediate (16e tetracoordinate Ir–H complex) responsible for the catalytic cycle. Experiments allowed explaining the effect of oxygen on the catalytic activity of phosphine-containing iridium siloxide complexes. The curing process of polysiloxanes catalyzed by iridium siloxide **II** and **IV** complexes occurs at a higher temperature (about 200 °C) than the same system catalyzed by Karstedt—diallylmaleate system (130 °C). The enthalpies of the reaction are comparable (−30 to −38 kJ/mol) for both catalysts but the inhibitor is not required for the iridium-catalyzed process.

Keywords: Silicones; Cross-linking; Hydrosilylation; Iridium complexes

1. Introduction

Molecular compounds incorporating TM–O–Si groups (where TM is transition metal) are of great interest, particularly as models of metal complexes immobilized on silica and silicate surfaces known to catalyze a variety of organic transformations [1–3]. Since 1982, more than 80 new well-defined TM-siloxide complexes including terminal and/or also bridging siloxy ligands have been synthesized and characterized by X-ray and spectroscopic methods to determine the molecular structure (for a recent review see ref. [1] and references therein). The properties of siloxide as ancillary ligand in the system TM–O–SiR_3 have been effectively utilized in molecular catalysis but predominantly by early transition metal complexes. Our recent study of the synthesis, structure and catalytic properties of rhodium and iridium dimeric and monomeric siloxide complexes indicate that those complexes can be very useful as catalysts and as catalysts precursors in a variety of reactions involving olefins, in particular silylative coupling (*trans*-silylation) [4], silylcarbonylation [5] and hydroformylation [6]. In addition, rhodium siloxide complexes appear to be much more effective than the respective chloro-complexes in hydrosilylation of a variety of olefins such as 1-hexene [7], vinylsilanes and polyvinylsiloxanes as well as allyl alkyl ethers [8].

The hydrosilylation processes are commonly used in catalytic cross-linking of polysiloxanes. However, descriptions in literature and patents are generally limited to systems involving well-known or modified platinum complexes in particular Karstedt's catalyst (for recent reviews see ref. [9]). Therefore, the aim of this paper is to examine iridium siloxide complexes as catalysts for hydrosilylation of model compounds as well as hydrosilylation of the vinylstopped polydimethylsiloxane in the presence of polyhydrosiloxane that leads to the network formation.

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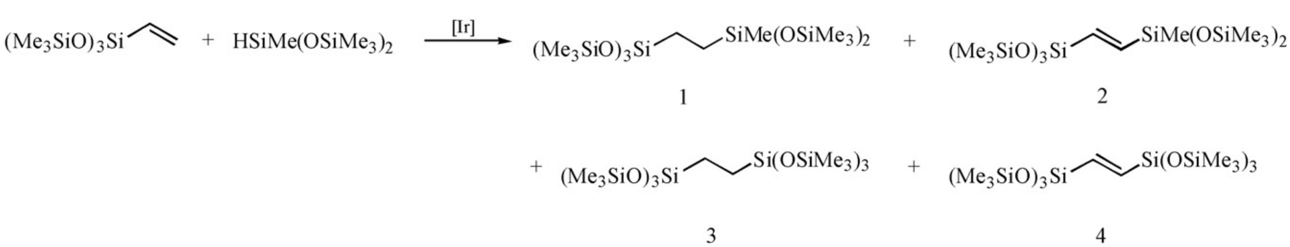
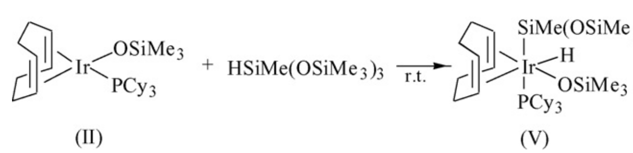
2. Results and discussion

The well-defined iridium siloxide complexes such as dimeric [{Ir(μ-OSiMe$_3$)(cod)}$_2$] (**I**) and monomeric [Ir(cod)(PCy$_3$)(OSiMe$_3$)] (**II**) and [Ir(CO)(PPh$_3$)$_2$(OSiMe$_3$)] (**III**), were synthesized according to a published procedure [4d,10]. Their X-ray structures were also reported previously [4d,10]. A new square-planar iridium siloxide complex consisting of two tricyclohexylphosphine ligands [Ir(CO)(PCy$_3$)$_2$(OSiMe$_3$)] (**IV**) was synthesized following the previously published procedure [10]. Those complexes were examined as catalysts of the model system involving reaction of vinyltris(trimethylsiloxy)silane with heptamethyltrisiloxane in the temperature range 110–120 °C which occurs according to the following equation:


(1)

The reaction leads to the formation of hydrosilylation product (1), which is accompanied by product of the dehydrogenative silylation (2) and, in some cases, respective products (3) and (4) (Table 1). The products (3) and (4) are result of preliminary H/vinyl exchange between reactants, followed by their hydrosilylation (3) and dehydrogenative silylation (4). This process is characteristic for TM catalyzed reactions of hydro- and vinyl-polysiloxanes [11].

All catalytic data are compiled in Table 1. The dimeric iridium siloxide complex **I** shows high yield under oxygen-free conditions but the hydrosilylation reaction is a strongly accompanied by the H/vinyl exchange of the substrates and yields also products (3) or (4). Interestingly, exposure of the complex **I** to air completely stops the hydrosilylation process. Contrary to the dimeric complex **I**, all phosphine monomeric complexes show much higher catalytic activity in the air than in oxygen-free conditions. This effect is a result of facile oxygenation and dissociation of phosphine ligand (more PCy$_3$ than PPh$_3$). ^{1}H NMR spectrum of the stoichiometric mixture of exemplary monomeric complex **II** and the model hydrotrisiloxane (HSiMe(OSiMe$_3$)$_2$) in C$_6$D$_6$ recorded at room temperature immediately after mixing the substrates, revealed the presence of doublet at $\delta = -13.19$ ppm and $J_{H\text{-}P} = 22$ Hz. It is a direct evidence of oxidative addition of Si–H bond to the complex **II** according to the Eq. (2) (complex **V**).


(2)

The ^{1}H NMR spectrum of the reaction mixture recorded after 3 h shows a doublet at $\delta = -6.85$ ppm and $J_{H\text{-}P} = 27$ Hz. A

Table 1
Irydium catalyzed hydrosilylation of vinyltris(trimethylsiloxy)slane with heptamethyltrisiloxane

Catalyst	Atmosphere	Temprature (°C)	Time (h)	Molar ratio [≡SiH]:[Ir]	Yield (%)		
					1	2	3 + 4
I	Argon	110	1	1:10^{-2}	72	3	9 + 10
			24	1:10^{-2}	70	2	0 + 17
	Air		24	1:10^{-2}	4	1	16 + 0
II	Argon	110	1	1:10^{-2}	78	3	3 + 11
			2	1:10^{-3}	95	3	0
			24	1:10^{-4}	10	1	0
	Air	80	24	1:10^{-4}	90	4	0
		110	1	1:10^{-4}	95	2	Traces
		110	1	1:10^{-5}	97	1	Traces
III	Argon	100	24	1:10^{-2}	44	22	0
	Air	120	24	1:5 × 10^{-3}	72	26	0
IV	Argon	120	24	1:10^{-3}	27	0	0
	Air	80	24	1:10^{-4}	57	1	0
		120	2	1:10^{-3}	81	9	0
		120	1	1:10^{-4}	81	9	0

[≡SiH]:[CH$_2$=CHSi≡] = 1:1.