

Effect of Buchwald-type ligands on platinum catalyzed hydrosilylation of vinyl terminated polydimethylsiloxane

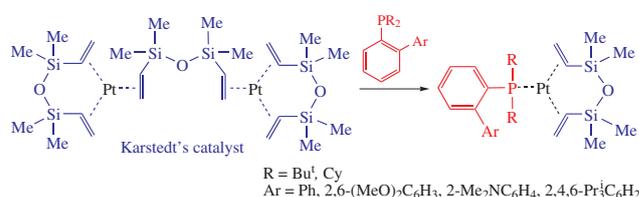
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The effect of Buchwald-type ligands on the platinum catalyzed hydrosilylation of vinyl-terminated polydimethylsiloxane has been studied by differential scanning calorimetry of platinum catalyst-containing silicone compositions. Dialkyl(biphenyl-2-yl)phosphines bearing bulky substituents at phosphorus atom are efficient inhibitors of the catalytic hydrosilylation process allowing one to increase the pot-life of silicone composition and to prevent the decomposition of the Pt-based catalyst.



Transition metal catalyzed hydrosilylation, which enables the addition of silicon hydrides across C–C, C–N, C–O and C–P multiple bonds, is an efficient method for the synthesis of organo-silicon compounds and one of the most important reactions in silicon chemistry, after the Rokhov process of dimethyldichlorosilane preparation.¹ The hydrosilylation process is widely used in industrial production of curable silicone compositions such as liquid rubbers, oils and gels. The development of novel addition-curable silicone materials requires novel catalysts with improved and adjustable parameters such as pot-life (time interval between mixing and gelation which is responsible for the usability of the materials when dosing the silicone composition after mixing the catalyst and the cross-linking copolymer) and stability. The hydrosilylation of vinyl-terminated polydimethylsiloxane (Vi-PDMS) occurs between silicon-bonded vinyl groups and Si–H fragments of hydrosiloxane oligomers. The use of Speier's (H_2PtCl_6) and Karstedt's $[\text{Pt}^0]$ catalysts is the major way for production of industrially important silicone materials by hydrosilylation.²

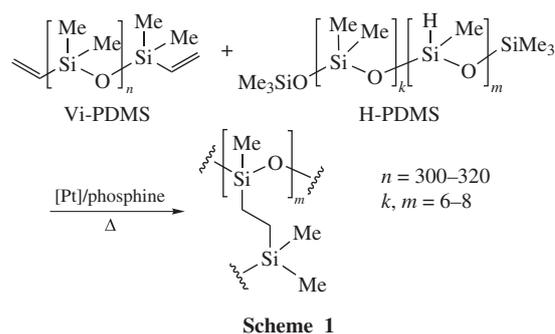
Different types of ligands capable of forming both labile and inert bonds with platinum center are currently used for the tuning of activity and selectivity of platinum based catalysts.¹ Up to present, many catalytically active compositions have been created based on the Karstedt's catalyst represented by general formula $[\text{Pt}_2(\text{D}2\text{V})_3]$, where D2V stands for 1,3-divinyltetramethyldisiloxane. The main types of ligands used for these purposes are represented by various phosphines,³ quinones,⁴ alkenes, alkynes and carbene-type ligands.^{5–7} Depending on the ligand nature the platinum complexes can produce different silicone materials with special properties.

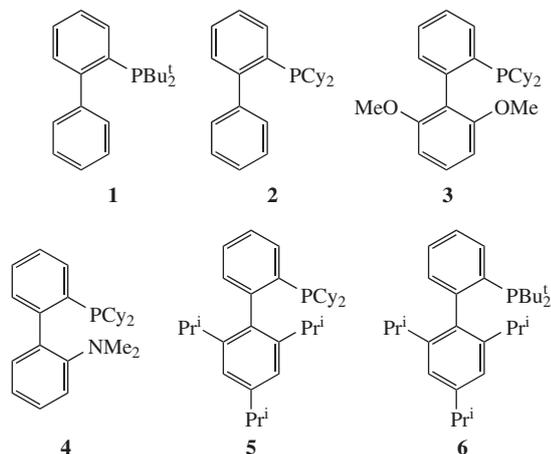
Important kinetic characteristics of the curing process such as pot-life of silicone composition, TOF and TON of the process can be easily adjusted by modification of the used catalyst. The activation of the catalyst is usually performed by heating (thermal cure) or UV-irradiation. However, the creation of smart and adjustable catalytic systems for hydrosilylation requires additional study focused on tuning of the structure and properties of

the used platinum catalysts in order to adjust their activity and selectivity for preparation of new types of the materials, including compositions for 3D-printing technologies.⁸

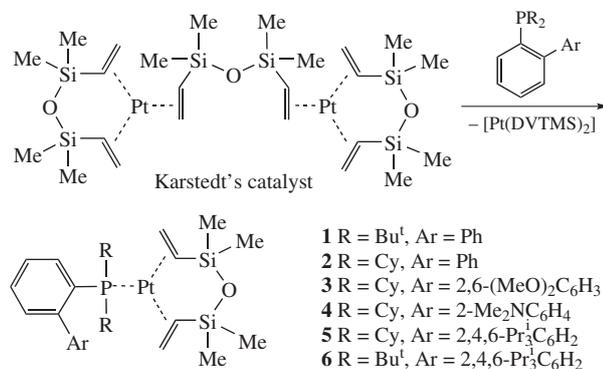
The pioneering works of Buchwald *et al.* regarding the use of dialkyl(biaryl)phosphines for Pd-catalyzed amination⁹ provided a breakthrough in synthetic organic chemistry.^{10–17} Specific electronic effects of these ligands, such as metal–aryl interaction, have been reported and studied using computational methods.^{18,19} However, no examples have been reported so far for the use of these ligands in platinum catalyzed reactions despite their advantages such as high sigma-donating strength of phosphorus atom, tunability of structural and electronic parameters in combination with high stability towards oxidation by atmospheric oxygen.¹⁵

In this work, we report the influence of Buchwald-type ligands on platinum catalyzed hydrosilylation of Vi-PDMS with trimethylsilyl-terminated poly(dimethylsiloxane-co-methylhydrosiloxane) (H-PDMS) (Scheme 1). The Buchwald-type ligands such as 2-(di-*tert*-butylphosphino)biphenyl **1**, 2-(dicyclohexylphosphino)biphenyl **2**, 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl **3**, 2-dicyclohexylphosphino-2'-(*N,N*-dimethylamino)biphenyl **4**, 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl **5** and 2-di-*tert*-butylphosphino-2',4',6'-triisopropylbiphenyl **6** have been tested.





Formation of platinum(0) complexes from dialkylbiarylphosphine ligands and the Karstedt's catalyst is shown in Scheme 2. The inhibiting properties of these Buchwald-type ligands have been investigated using the Vi-PDMS/H-PDMS system (see Scheme 1) by differential scanning calorimetry (DSC) and evaluation of their catalytic activity compared to standard Karstedt's catalyst.



Scheme 2

Note that the starting temperature (T_{onset}) and the peak temperature (T_{peak}) of the curing process are important parameters for the optimization of curing temperature of silicone composition.²⁰ We have found that addition of Buchwald-type ligands to the reaction mixture containing Pt-catalyst in molar ratio ligand:Pt of 1 : 1 increases a pot-life of the catalytic composition compared to the Karstedt's catalyst (Table 1, Figure 1). It was also revealed that addition of phosphine co-ligand increased the enthalpy of the catalytic hydrosilylation process.

According to the obtained data, the addition of Buchwald-type ligand to the system containing Karstedt's catalyst leads to

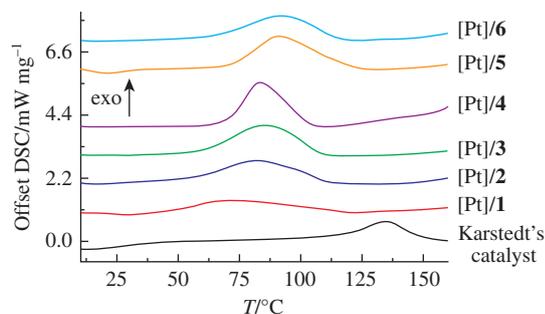


Figure 1 DSC curves (10 K min⁻¹, nitrogen) of the reaction mixtures containing Vi-PDMS and H-PDMS in the presence of Karstedt's catalyst with and without Buchwald-type ligands.

Table 1 Effect of the Buchwald-type ligands on the catalytic hydrosilylation catalyzed by platinum based Karstedt's catalyst.

Entry	Co-ligand	Pot-life at 25 °C/min	$T_{\text{onset}}/^{\circ}\text{C}$	$T_{\text{peak}}/^{\circ}\text{C}$	$-\Delta H_{\text{reaction}}/\text{J g}^{-1}$
1	1	10	46	72	8.5
2	2	108	58	82	9.7
3	3	53	70	93	10.8
4	4	120	71	91	13.0
5	5	64	62	86	12.4
6	6	101	70	84	12.7
7	–	<6	17	134	7.9

the increase in a pot-life of the catalytic system. The ³¹P NMR data show that addition of tertiary phosphines results in decomposition of the Karstedt's catalyst and formation of new platinum(0) complexes bearing phosphine ligands in the coordination sphere (*cf.* ref. 3). Thus, after addition of phosphine **6** (δ_{P} 21.24 ppm) to Karstedt's catalyst, two new signals with δ_{P} 92.65 ppm ($^1J_{\text{Pt}}$ 3607 Hz) and δ_{P} 91.40 ppm ($^1J_{\text{Pt}}$ 3651 Hz) with integral intensity 2 : 1 were observed in ³¹P NMR spectra. In the ¹H NMR spectrum, the signals for the vinyl groups of D2V in the initial form of Karstedt's catalyst have been shifted from δ_{H} 2.5–3.7 ppm ($^2J_{\text{Pt-H}}$ 4.1–7.3 Hz) to δ_{H} 2.0–3.0 ppm ($^2J_{\text{Pt-H}}$ 2.0–3.8 Hz).

It was of interest to investigate the [Pt]/ligand concentration on catalytic activity and stability of the catalyst. The obtained results revealed that the pot-life of catalytic composition decreased on raising the catalyst concentration, and the catalytic reaction was found to have first order (Figure 2). In the related investigation of the dependence of initial and total reaction rate of hydrosilylation of unsaturated hydrocarbons on concentration of active platinum in solution,²¹ it was found that of the total reactant conversion was reduced upon increase in platinum concentration higher than 125 ppm due to the formation of low-reactive colloidal platinum. However, in our experiments, the presence of Buchwald-type ligands hampered formation of colloidal platinum and hence, the decomposition of the catalyst.

The use of increased phosphine/Pt molar ratio as compared to 1 : 1 leads to prolongation of pot-life of the catalytic system. Thus, for catalytic mixture [Pt]/**4** with 1 : 3 ratio, the dramatic increase in pot-life (up to 72 h) was observed, while the peak temperature was shifted up to 113 °C ($-\Delta H_{\text{reaction}}$ 12.6 J g⁻¹) (Figure S1, see Online Supplementary Materials).

In summary, the use of Buchwald-type co-ligands in the hydrosilylation of Vi-PDMS and H-PDMS with the Karstedt's catalyst allows one sufficiently increase a pot-life of polymeric silicone compositions. Application of these ligands provides high stability of thus formed catalysts at high concentrations depriving formation of platinum colloids. This can be explained by specific steric and electronic effects of coordinated Buchwald-type ligands on the rate-determining step of the alkene insertion into the formed intermediate Pt–H bond as it was shown for Pd-catalyzed C–C coupling reaction.²²

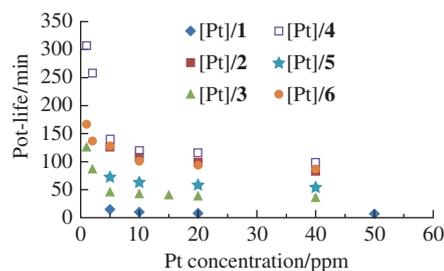


Figure 2 Pot-life of catalytic composition vs. platinum concentration.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.07.035.

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