Electronic supplementary materials *Mendeleev Commun*., 2019, **29**, 458–460

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

Ruslan Yu. Lukin, Dmitry A. Emelyanov, Aleksander D. Kachmarzhik, Aleksander V. Sukhov, Oleg G. Sinyashin and Dmitry G. Yakhvarov

All manipulations with air-sensitive compounds were carried out under dry nitrogen using Schlenk techniques. Solvents were dried by standard methods and freshly distilled before use. NMR spectra were recorded with a multinuclear Bruker Avance-III 400 MHz spectrometer at 300.1 (^{1}H), 75.5 (^{13}C) and 121.5 (^{31}P) MHz in $CDCl_3$. Chemical shifts (δ) are given in ppm and are referenced to tetramethylsilane for ^{1}H and ^{13}C NMR and to H_3PO_4 (85%) for ^{31}P NMR unless indicated otherwise. The curing process was monitored by Differential Scanning Calorimetry (DSC). All experiments were carried out on DSC 214 Polyma (Netzsch GmbH). The DSC instrument was calibrated under the standard procedure according to ASTM E967-18. The heating rate for each experiment was 10 K min^{-1} in an open aluminum crucible with the lid (hole) under the nitrogen atmosphere with the gas flow of 75 ml min^{-1}. The calibration was complete for the sensitivity and the temperature of the sensor. The reference crucible was exactly the same as the sample ones. To achieve the statement of accuracy, the melting points of four highly pure metals (In, Sn, Bi, Zn) were used as well as the phase transition of some organic compounds (adamantane $C_{10}H_{16}$) under the conditions of the experiments (the same atmosphere, gas flow, crucible type, heating rate). In order to exclude the baseline of the instrument before each experiment, the correction procedure was applied. In addition, the thermal delay and the constant of the instrument were excluded with the procedure called TaUR calibration in order to avoid the overlapping effect. The calibration samples were close to the experiment ones. Analysis conditions (DSC): keeping for 1.0 min at 0°C, heating 0→200°C at 10 K min^{-1}, then cooling to room temperature.

The chemicals were obtained from the following sources. Buchwald ligands 2-(di-*tert*-butylphosphino)biphenyl (JohnPhos, **1**), 2-(dicyclohexylphosphino)biphenyl (CyJohnPhos, **2**), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (SPhos, **3**), 2-dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl (DavePhos, **4**), 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (XPhos, **5**), 2-di-*tert*-butylphosphino-2′,4′,6′-triisopropylbiphenyl (tBuXPhos, **6**), trimethylsilyl

terminated poly(dimethylsiloxane-co-methylhydrosiloxane) (H-PDMS) (M_n = 950, molar Si-H content 50%), vinyl-terminated polydimethylsiloxane (Vi-PDMS) (M_n = 25000) (CAS Number 68083-19-2) and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane (D2V) were purchased from Sigma-Aldrich. The solvents were obtained from "Component Reaktiv" company (Russia).

Preparation of the Karstedt's catalyst. The catalyst was prepared by modified literature procedure [L. N. Lewis, Stein J., Y. Gao, R. E. Colborn and G. Hutchins, *Platinum Metals Review,* 1997, **41**, 66]. Acid H_2PtCl_6 was added to D2V in molar ratio 1:22. After heating at 59 °C and neutralization by $NaHCO_3$, the solution was concentrated under vacuum and diluted in xylene.

*Preparation of [Pt]/**1** system.* A solution containing 2-(di-*tert*-butylphosphino)biphenyl **(1)** (5.97 mg, 0.02 mmol) in toluene (0.9 ml) was added to a solution of Karstedt's catalyst (0.1 ml) containing 0.2 M of platinum in D2V. The molar ratio phosphine ligand/Pt was 1:1. The resulting mixture was used for catalytic tests. ^{31}P NMR: δ = 59.91 ($^1J_{P\text{-}Pt}$ = 3888 Hz)

*Preparation of [Pt]/**2** system.* A solution containing 2-(dicyclohexylphosphino)biphenyl **(2)** (7.01 mg, 0.02 mmol) in toluene (0.9 ml) was added to a solution of Karstedt's catalyst (0.1 ml) containing 0.2 M of platinum in D2V. The molar ratio phosphine ligand/Pt was 1:1. The resulting mixture was used for catalytic tests. ^{31}P NMR: δ = 33.50 ($^1J_{P\text{-}Pt}$ = 3543 Hz)

*Preparation of [Pt]/**3** system.* A solution containing 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl **(3)** (8.21 mg, 0.02 mmol) in toluene (0.9 ml) was added to a solution of Karstedt's catalyst (0.1 ml) containing 0.2 M of platinum in D2V. The molar ratio phosphine ligand/Pt was 1:1. The resulting mixture was used for catalytic tests. ^{31}P NMR: δ = 33.50 ($^1J_{P\text{-}Pt}$ = 3543 Hz).

*Preparation of [Pt]/**4** system.* A solution containing 2-dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl **(4)** (7.87 mg, 0.02 mmol) in toluene (0.9 ml) was added to a solution of Karstedt's catalyst (0.1 ml) containing 0.2 M of platinum in D2V. The molar ratio phosphine ligand/Pt was 1:1. The resulting mixture was used for catalytic tests. ^{31}P NMR: δ = 40.62 ($^1J_{P\text{-}Pt}$ = 3609 Hz).

*Preparation of [Pt]/**5** system.* A solution containing 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl **(5)** (9.53 mg, 0.02 mmol) in toluene (0.9 ml) was added to a solution of Karstedt's catalyst (0.1 ml) containing 0.2 M of platinum in D2V. The molar ratio phosphine ligand/Pt was 1:1. The resulting mixture was used for catalytic tests. ^{31}P NMR: δ = 45.19 ($^1J_{P\text{-}Pt}$ = 3689 Hz), δ = 44.44 ppm ($^1J_{P\text{-}Pt}$ = 3451 Hz).

*Preparation of [Pt]/**6** system.* A solution containing 2-di-*tert*-butylphosphino-2′,4′,6′-triisopropylbiphenyl **(6)** (8.49 mg, 0.02 mmol) in toluene (0.9 ml) was added to a solution of Karstedt's catalyst (0.1 ml) containing 0.2 M of platinum in D2V. The molar ratio phosphine ligand/Pt was 1:1. The resulting mixture was used for catalytic tests. ^{31}P NMR: δ = 92.28 ($^{1}J_{P\text{-}Pt}$ = 3658 Hz), δ = 91.14 ppm ($^{1}J_{P\text{-}Pt}$ = 3635 Hz).

Catalytic tests of hydrosilylation. The curing process was studied in the system containing Vi-PDMS and H-PDMS. The molar ratio [SiH]/[SiCH = CH_2] was 2:1, platinum concentration was 10 ppm of atomic platinum by mass.

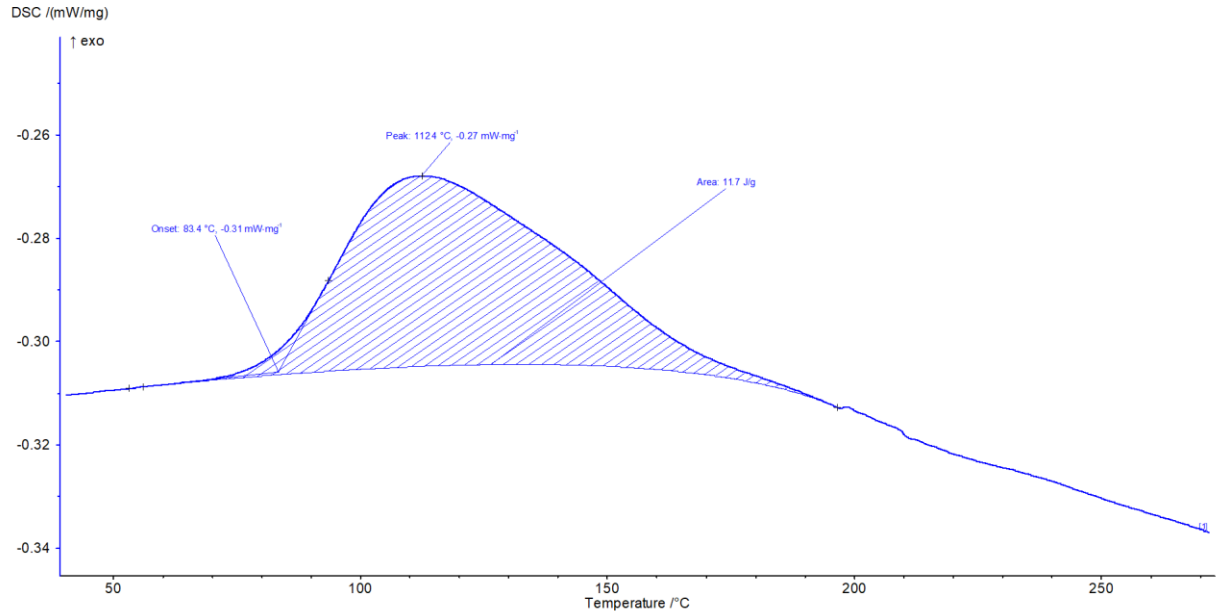

Figure S1 DSC curve of the mixture containing [Pt]/**4** (1:3 molar ratio).