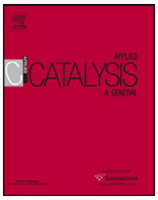
Applied Catalysis A: General 380 (2010) 105–112

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata



Tris(triorganosilyl)phosphites—New ligands controlling catalytic activity of Pt(0) complex in curing of silicone rubber

Ireneusz Kownacki[a], Bogdan Marciniec[a,*], Karol Szubert[a], Maciej Kubicki[a], Magdalena Jankowska[a], Helmut Steinberger[b], Sławomir Rubinsztajn[c]

[a] Adam Mickiewicz University, Faculty of Chemistry, Grunwaldzka 6, 60-780 Poznan, Poland
[b] Momentive Performance Materials, D-51368 Leverkusen, Germany
[c] GE Global Research Center, 1 Research Circle, Schenectady, NY 12309, USA

ARTICLE INFO

Article history:
Received 11 January 2010
Received in revised form 15 March 2010
Accepted 18 March 2010
Available online 25 March 2010

Keywords:
Hydrosilylation
Karstedt's catalyst
Platinum complexes
Silylphosphites
Curing
Silicones

ABSTRACT

Applying novel and efficient method, new tris(triorganosilyl)phosphites were synthesized and further used for the preparation of new well-defined platinum complexes [Pt(DVTMDS){P(OSiR$_3$)$_3$}] (DVTMDS = (H$_2$C=CHSiMe$_2$)$_2$O, R$_3$ = Si$_7$O$_9$(^{i}Oct)$_7$, ^{i}Pr$_3$, MePh$_2$, Ph$_3$, (O^{t}Bu)$_3$, (OSiMe$_3$)$_3$) which were well characterized by spectroscopic methods. Structures of two platinum(0) complexes, [Pt{η^4-(H$_2$C=CHSiMe$_2$)$_2$O}{P(OSiPh$_3$)$_3$}] (**10**) and [Pt{η^4-(H$_2$C=CHSiMe$_2$)$_2$O}{P(OSi(O^{t}Bu$_3$)$_3$}] (**11**) were determined by X-ray analysis. The new complexes proved to be very effective catalysts of a cross-linking of silicones *via* hydrosilylation at elevated temperature with relatively short cure time and the enthalpy of network formation similar to that of Pt-Karstedt's/DAM (DAM = diallyl maleate) catalytic system. Additionally, the catalyzed silicone formulation had sufficiently long pot-life at room temperature.

1. Introduction

Derivatives of phosphorus acids having at least one acidic hydrogen atom replaced by organosilyl group belong to the class of compounds called silyl esters of phosphorus acid. Synthetic methods and application of various silyl esters of phosphorus acid have been widely reviewed by Chojnowski [1].

We are interested in phosphorus derivatives containing three organosilicon groups bonded to phosphorus atom *via* three oxygen atoms. Such compounds can be obtained by silylation of phosphorus acid with different silylation agents, e.g. tris(trimethylsilyl)phosphite produced in the reaction of phosphorus acid H$_3$PO$_3$ with chlorotrimethylsilane (TMSCl). Introduction of two silyl groups occurs easily without any HCl acceptor. However, incorporation of the third group requires an use of amine or another reagent, which transforms the diester into P(III) tautomeric form [2–4]. Reaction of trialkyl phosphites with three equivalents of chlorotriorganosilane was reported as an efficient synthetic method for the preparation of tris(triorganosilyl)phosphites [5]. Preparation of monosilyl esters of P(III) *via* replacement of the chlorine substituent in chlorodiorganophosphines by potassium silanolate was also described [6].

Silyl esters of phosphorus acid found a wide range of applications in the areas of organic, inorganic and bioorganic chemistry [7–19]. Trimethylsilyl derivatives were used as efficient reagents in synthesis of various organophosphorus compounds, e.g. using Arbuzov reaction [7–10] or the Perkow reaction [11].

A complex of platinum(0) with 1,3-divinyltetramethyldisiloxane, so-called Karstedt's catalyst, is commercially available, high activity catalyst for vulcanization of silicone elastomers *via* hydrosilylation. Majority of commercial applications require an addition of inhibitors, which temporarily diminish high catalytic activity of the Karstedt's catalyst. The unsaturated diesters, e.g. maleates and fumarates, are the most important and commonly used class of the platinum inhibitors. Their inhibition properties were described in many papers and patents [20–23]. Triorganophosphites were also reported as efficient inhibitors of Pt-catalyzed hydrosilylation process [24]. Well-defined platinum complexes with triorganophosphites were also employed as silicon fluids vulcanization catalysts [24f–h, 25] and appeared to be very efficient for this such purpose.

Many Pt(0) complexes prepared by treatment of the Karstedt's catalyst with various phosphines [26] have been isolated and used as catalysts of the hydrosilylation process. Other Pt(0, +2) com-

---

* Corresponding author. Tel.: +48 061 8291366; fax: +48 061 8291508.
E-mail address: bogdan.marciniec@amu.edu.pl (B. Marciniec).

0926-860X/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2010.03.041

plexes with phosphirane [27,28] chelating ligands also appeared selective and efficient in the hydrosilylation reaction.

Our previous studies on the synthesis, properties and application of various triorganophosphites as inhibitors that control the catalytic activity of platinum Karstedt's complex in the cross-linking of silicone fluids as well as useful starting phosphorus based ligands for the preparation of platinum(0) complexes, new efficient catalysts of curing process [24f–h], encouraged us to develop the new type of phosphorus ligands containing organometalloid substituents. Therefore, the aim of this work was to prepare several novel tris(triorganosilyl)phosphites of the general formula $P(OSiR_3)_3$ and platinum(0) complexes with these silylphosphite ligands $[Pt(DVTMDS)\{P(OSiR_3)_3\}]$ as well as to study their efficiency in catalysis of cross-linking process of the vinyl-terminated polydimethylsiloxane with polyhydrosiloxane.

2. Experimental

All syntheses and manipulations were carried out under argon using standard Schlenk's and vacuum techniques. ^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR spectra were recorded on a Varian Gemini 300 VT and Varian Mercury 300 VT spectrometers in benzene-d_6.

The chemicals were obtained from the following sources: chlorosilanes, PCl_3, NaH and benzene-d_6 from Aldrich, Karstedt's catalyst from Aldrich and GE Silicones, polyhydromethylsiloxane (1.0 wt% of SiH), vinyl-terminated polydimethylsiloxane (0.0248 wt% of $-CH{=}CH_2$) from GE Silicones, solvents from POCH Gliwice (Poland). The curing process was studied in a system consisting of vinyl-terminated polydimethylsiloxane and polyhydromethylsiloxane as a cross-linker. The standard formulation had $([\equiv SiH]/[\equiv SiCH{=}CH_2] = 1.93$ and the platinum concentration was $[\equiv SiH]:[Pt] = 1:10^{-5}$. The progress of the curing process was monitored by Differential Scanning Calorimetry (DSC) test method. DSC measurements were made using a DSC 204 NETCH. 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 20 to 220 °C at 10 °C/min, cool from 250 to 30 °C at 20 °C/min. DSC experiments were made in triplicate for each test.

2.1. X-ray structure determination

Colourless single crystals of the compounds **10** and **11** were grown by crystallization in low temperature, where toluene for **10** and pentane **11** were used. Diffraction data were collected at 100 K by the ω-scan on a KUMA KM4CCD diffractometer [29] with graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å). The data were corrected for Lorentz-polarization effects as well as for absorption [30]. Accurate unit-cell parameters were determined by the least-squares fit of 30553 (**10**) and 5563 (**11**) reflections of highest intensity, chosen from the whole experiment. The structures were solved with SHELXS97 [31] and refined with the full-matrix least-squares procedure on F^2 by SHELXL97 [32]. Scattering factors incorporated in SHELXL97 were used. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were placed geometrically, in idealized positions, and refined as rigid groups, U_{iso} of hydrogen atoms were set as 1.2 (1.3 for methyl groups) times U_{eq} of the appropriate carrier atom. In **11**, one of the *t*-Bu groups is disordered; the site occupation factors of these groups refined at 0.55(1) and 0.45(1). Relevant crystal data are listed in Table 1, together with refinement details.

2.1.1. Supplementary material

Crystallographic data (excluding structure factors) for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, Nos. CCDC-664896 (**10**) and CCDC-664897 (**11**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44(1223)336-033, e-mail:deposit@ccdc.cam.ac.uk, or www: www.ccdc.cam.ac.uk.

Table 1
Crystal data, data collection and structure refinement.

Compound	**10**	**11**
Formula	$C_{62}H_{63}O_4PPtSi_5$	$C_{44}H_{99}O_{13}PPtSi_5$
Formula weight	1238.63	1202.74
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2/c$
a (Å)	15.4224(5)	19.782(2)
b (Å)	13.0054(4)	13.4645(14)
c (Å)	28.5569(9)	23.0571(18)
β (°)	96.002(3)	98.248(7)
V (Å^3)	5696.4(3)	6077.8(10)
Z	4	4
D_x (g cm^{-3})	1.444	1.314
$F(000)$	2520	2520
μ (mm^{-1})	2.643	2.484
Crystal size (mm)	0.3 × 0.2 × 0.15	0.15 × 0.1 × 0.1
T (K)	100(1)	100(1)
Θ range (°)	2.42–29.81	2.66–25.00
hkl range	$-21 \le h \le 16$ $-17 \le k \le 16$ $-39 \le l \le 37$	$-23 \le h \le 19$ $-15 \le k \le 14$ $-27 \le l \le 27$
Reflections:		
Collected	56426	26371
Unique (R_{int})	14924 (0.041)	10226 (0.088)
With $I > 2\sigma(I)$	10883	5176
Number of parameters	662	629
$R(F)$ $[I > 2\sigma(I)]$	0.0332	0.041
$wR(F^2)$ $[I > 2\sigma(I)]$	0.0690	0.047
$R(F)$ [all data]	0.0589	0.101
$wR(F^2)$ [all data]	0.0738	0.051
Goodness of fit	1.013	0.72
max/min $\Delta\rho$ (e Å^{-3})	1.78/−0.86	0.88/−0.74
CCDC deposition number	CCDC-664896	CCDC-664897

2.2. Descriptions of syntheses

2.2.1. Procedures for syntheses of silanols

*2.2.1.1. Synthesis of tri-iso-propylsilanol (**A**).* A solution of 5.76 g (0.057 mol) of triethylamine in 150 mL of water and 300 mL of diethyl ether were placed in a 750 mL two-neck, round-bottomed flask, equipped with a magnetic stirrer and a thermometer. The reaction flask was cooled by an ice bath. 10 g (0.052 mol) of tri-*iso*-propylchlorosilane was added dropwise to a vigorously stirred reaction mixture at 0 °C. After 1 h, the reaction mixture was transferred into the 1L separatory-funnel and the water layer was removed. The organic layer was washed twice with DI water. The ether solution was finally dried over 30 g of anhydrous magnesium sulfate. Solvent was evaporated under reduced pressure and the product obtained was used toward the synthesis of tris(tri-*iso*-propylsilyl)phosphite without additional purification. Yield 8.23 g (91%).

*2.2.1.2. Synthesis of methyldiphenylsilanol (**B**).* This compound was prepared in analogous way as tri-*iso*-propylsilanol, starting from 4.76 g (47 mmol) of NEt_3, 10 g (43 mmol) of chloromethyldiphenylsilane ($SiClMe_2Ph$). The product obtained was purified by distillation under vacuum using the trap-to-trap technique. Yield 5.36 g (82%).

*2.2.1.3. Synthesis of tris(trimethylsiloxy)silanol (**C**).* This compound was prepared analogously as described for the silanol A, starting from 3.36 g (33 mmol) of NEt_3, 10 g (30 mmol) of chlorotris(trimethylsiloxy)silane ($SiCl(OSiMe_3)_3$). The product obtained was used for the next step without additional purification. Yield 8.92 g (95%).

2.2.2. *Procedures for syntheses of tris(triorganosilyl)phosphites (compounds **1–6**)*

*2.2.2.1. Synthesis of phosphorussilsesquioxane (**1**).* The solution of $Si_7O_9(OH)_3(^iOct)_7$ (POSS-*iso*-Octyl, POSS® = Polyhedral Oligomeric Silsesquioxane) (5 g, 4.22 mmol) in 30 mL of dried and deoxidized THF was added dropwise to a vigorously mix suspension of NaH (0.608 g, 25.3 mmol) in 10 mL of THF at room temperature under dry argon atmosphere over 20 min. The reaction was carry on for 24 h at room temperature. After this time the solution of sodium POSS-*iso*-Oct-trisilanolate was filtered off by a cannula system. PCl_3 (0.562 g, 4.09 mmol) was added to the solution of sodium POSS-*iso*-Oct-trisilanolate and the mixture was stirred for 24 h at room temperature, and subsequently stirred for 2 h at 50 °C. At the next step the reaction mixture was cooled to room temperature, solvent was removed under reduced pressure, and hexane was added. The suspension obtained was filtered off by a cannula system and the solvent was evaporated under reduced pressure. Phosphorussilsequioxane was obtained with a yield of 94% (4.66 g).

Anal. calc. for $C_{56}H_{119}O_{12}PSi_7$ C 55.49; H 9.90; found C 58.58; H 10.05. ^1H NMR (300 MHz, C_6D_6, 300 K) δ (ppm) = 2.24 (bm, 7H, –CH–); 1.8–0.8 (bm, 112H, H–). ^{13}C NMR (75.42 MHz, C_6D_6, 300 K) δ (ppm) = 54.79, 54.39, 53.91; 31.03, 30.08, 29.28; 25.47, 25.18, 24.85, 23.94. ^{31}P NMR (121.47 MHz, C_6D_6, 300 K) δ (ppm) = 84.64.

2.2.3. *Synthesis of tris(tri-iso-propylsilyl)phosphite $P(OSi^iPr_3)_3$ (**2**)*

The tri-*iso*-propylsilanol (**A**) (5 g, 28.7 mmol) was added dropwise to a vigorously mix suspension of NaH (1.00 g, 42 mmol) in 50 mL of THF at room temperature under dry argon atmosphere over 20 min. The reaction was conducted for 24 h at room temperature. Subsequently, the reaction mixture was filtered off by a cannula system. PCl_3 (1.24 g, 9.08 mmol) was added to the solution of sodium tri-*iso*-propylsilanolate and the mixture was stirred for 24 h at 60 °C. At the next step, the content was cooled to room temperature and the solvent was removed under reduced pressure, then the pentane was added. The suspension obtained was filtered off by a cannula system, and solvent was evaporated under reduced pressure giving tris(tri-*iso*-propylsilyl)phosphite as colorless oil. Yield 4.70 g (94%).

Anal. calc. for $C_{27}H_{63}O_3PSi_3$ C 58.85; H 11.52; found C 58.91; H 11.61. ^1H NMR (300 MHz, C_6D_6, 300 K) δ (ppm) = 1.21 (d, 54H, –Me); 1.11, 1.04 (m, 9H, $SiCHMe_2$). ^{13}C NMR (75.42 MHz, C_6D_6, 300 K) δ (ppm) = 18.48, 18.45 (–Me), 13.88 ($SiCHMe_2$). ^{31}P NMR (121.47 MHz, C_6D_6, 300 K) δ (ppm) = 110.18, ^{29}Si NMR (59.59 MHz, C_6D_6, 300 K) δ (ppm) = 15.23 (J_{Si-P} = 14.66 Hz).

2.2.4. *Synthesis of tris(methyldiphenylsilyl)phosphite $P(OSiMePh_2)_3$ (**3**)*

This compound was prepared in analogous way as compound **2**, starting from 3 g (14 mmol) of methyldiphenylsilanol (**B**), 0.67 g (28 mmol) of NaH and 0.6 g (4.37 mmol) of PCl_3. After addition of PCl_3 mixture was stirred for 24 h at 55 °C. The suspension obtained was filtered off by a cannula system, and solvent was evaporated under reduced pressure giving tris(methyldiphenylsilyl)phosphite as white solid. Yield 2.67 g (91%).

Anal. calc. for $C_{39}H_{39}O_3PSi_3$ C 69.81; H 5.86; found C 69.88; H 5.95. ^1H NMR (300 MHz, C_6D_6, 300 K) δ (ppm) = 7.54 (m), 7.36 (m) (30H, *o,m,p*-Ph); 0.61 (s, 9H, $SiMePh_2$). ^{13}C NMR (75.42 MHz, C_6D_6, 300 K) δ (ppm) = 137.44; 133.87; 129.46; 127.62 (–Ph); −0.44 (–Me). ^{31}P NMR (121.47 MHz, C_6D_6, 300 K) δ (ppm) = −13.61. ^{29}Si NMR (59.59 MHz, C_6D_6, 300 K, INEPT) δ (ppm) = −7.10.

2.2.5. *Synthesis of tris(triphenylsilyl)phosphite $P(OSiPh_3)_3$ (**4**)*

The solution of triphenylsilanol (5 g, 18 mmol) in 50 mL of dried and deoxidized THF was added dropwise to a vigorously mix suspension of NaH (0.8 g, 36 mmol) in 20 mL of THF at room temperature under dry argon atmosphere over 20 min. The reaction was conducted for 2 h at 50 °C. After this time the mixture was filtered off by a cannula system. PCl_3 (0.745 g, 5.42 mmol) was added to the solution of sodium triphenylsilanolate and the mixture was stirred for 12 h at 60 °C. At the next step the content was cooled to room temperature, THF was removed under reduced pressure, and benzene was added. The suspension obtained was warmed up to 65 °C and filtered off by cannula system, and solvent was evaporated under reduced pressure. Subsequently, Tris(triphenylsilyl)phosphite was washed twice with hexane and dried under vacuum. Yield 4.37 g (94%).

Anal. calc. for $C_{54}H_{45}O_3PSi_3$ C 75.67; H 5.29; found C 75.72; H 5.40. ^1H NMR (300 MHz, C_6D_6, 300 K) δ (ppm) = 7.60 (d), 7.18 (m), 7.06 (t), (45H, *o,m,p*-Ph). ^{13}C NMR (75.42 MHz, C_6D_6, 300 K) δ (ppm) = 136.03; 136.01; 134.74; 130.19; 130.88; 128.12. ^{31}P NMR (121.47 MHz, C_6D_6, 300 K) δ (ppm) = 112.49. ^{29}Si NMR (59.59 MHz, C_6D_6, 300 K) δ (ppm) = 13.28 (d, J_{Si-P} = 10 Hz).

2.2.6. *Synthesis of tris(tri-tert-butoxysilyl)phosphite $P(OSi(O^tBu)_3)_3$ (**5**)*

This compound was prepared in analogous way as compound **2**, starting from 5 g (19 mmol) of tri-*tert*-butoxysilanol ($Si(OH)(O^tBu)_3$), 0.91 g (38 mmol) of NaH and 0.83 g (6.02 mmol) of PCl_3. After addition of PCl_3 the mixture was stirred for 24 h at 55 °C. The suspension obtained was filtered off by a cannula system, and then solvent was evaporated under reduced pressure giving tris(tri-*tert*-butoxysilyl)phosphite as white solid. Yield 4.55 g (92%).

Anal. calc. for $C_{36}H_{81}O_{12}PSi_3$ C 52.65; H 9.94; found C 52.70; H 10.06. ^1H NMR (300 MHz, C_6D_6, 300 K) δ (ppm) = 1.52 (81H, O^tBu). ^{13}C NMR (75.42 MHz, C_6D_6, 300 K) δ (ppm) = 74.89; 74.41; 74.16; 73.01; 72.86 ($-O-\underline{C}Me_3$); 31.2; 31.30; 31.32; 31.39; 31.67 (–Me). ^{31}P NMR (121.47 MHz, C_6D_6, 300 K) δ (ppm) = 109.62.

2.2.7. *Synthesis of tri(tris(trimethylosiloxy)silyl)phosphite $P(OSi(OSiMe_3)_3)_3$ (**6**)*

This compound was prepared analogously as described for 2, starting from 5 g (16 mmol) of $Si(OH)(OSiMe_3)_3$ (**C**), 0.57 g (24 mmol) of NaH and 0.68 g (5.0 mmol) of PCl_3. After addition of PCl_3 mixture was stirred for 24 h at 60 °C. The suspension obtained was filtered off by a cannula system, and then the solvent was evaporated under reduced pressure giving tri(tris(trimethylsiloxy)silylphosphite as colourless oil. Yield 4.59 g (95%).

Anal. calc. for $C_{27}H_{81}O_{12}PSi_{12}$ C 33.57; H 8.45; found C 33.63; H 8.54. ^1H NMR (300 MHz, C_6D_6, 300 K) δ (ppm) = 0.32 (s, 81H, –Me). ^{13}C NMR (75.42 MHz, C_6D_6, 300 K) δ (ppm) = 2.36 (–Me). ^{31}P NMR (121.47 MHz, C_6D_6, 300 K) δ (ppm) = 111.73. ^{29}Si NMR (59.59 MHz, C_6D_6, 300 K, INEPT) δ (ppm) = 11.89 (J_{Si-P} = 60.27 Hz).

2.2.8. *General procedure for synthesis of complexes (**7–12**)*

Complexes **7–12** were synthesized under inert atmosphere by reacting the calculated amounts of Karstedt's catalysts and corresponding silylphosphite **1–6** in molar ratio $[Pt]:[P(OSi{\equiv})_3] = 1:1.02$. Reactions were conducted for 24 h at room temperature for complexes **7–9**, **11** and **12**. After this time the mixtures were filtered off by a cannula system and solvent was evaporated under vacuum for 24 h at 50 °C. Solid products were three times washed with pentane by decantation at −70 °C.

2.2.9. *Analytical data of platinum(0) complexes*

*2.2.9.1. Complex $[Pt\{\eta^4-(H_2C{=}CHSiMe_2)_2O\}\{P(Si_7O_{12}(^iOct)_7\}]$ (**7**).* Yield 1.21 g (98%). Anal. calc. for $C_{66}H_{143}O_{13}PPtSi_9$ C 48.82; H

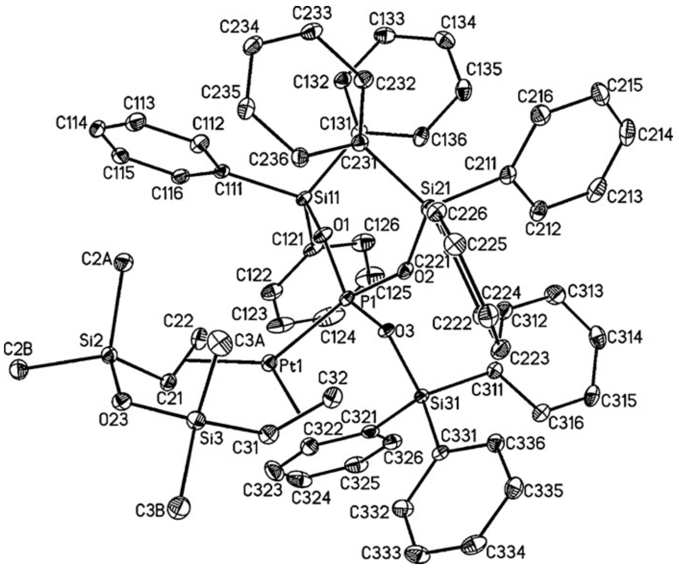


Fig. 1. Anisotropic ellipsoid representation of complex **10**. The ellipsoids are drawn at 50% probability level, hydrogen atoms are omitted for clarity.

8.88; found C 48.90; H 9.03. ^{1}H NMR (300 MHz, C_6D_6, 300 K) δ (ppm) = 2.43 (m), 3.4–2.8 (m) (6H, –CH=CH$_2$); 2.2 (bm, 7H, –CH–); 1.7–0.83 (bm, 112H, H-aliphatic); 0.53 (s), 0.516 (s) (6H, –Me); −0.13(m), −0.25(m) (6H, –Me). ^{13}C NMR (75.42 MHz, C_6D_6, 300 K) δ (ppm) = 57.55, 57.25, 56.47, 55.84 (–CH=CH$_2$); 54.34, 53.90; 31.08, 30.08, 29.28; 25.46, 23.94; 1.44, −2.19, −2.04. ^{31}P NMR (121.47 MHz, C_6D_6, 300 K) δ (ppm) = 83.12 ($J_{\text{P–Pt}}$ = 6687.6 Hz).

*2.2.9.2. Complex [Pt{η^4-(H$_2$C=CHSiMe$_2$)$_2$O}{P(OSi^{i}Pr$_3$)$_3$}] (**8**).* Yield 1.63 g (98%). Anal. calc. for $C_{35}H_{81}O_4PPtSi_5$ C 45.08; H 8.76; found C 45.13; H 8.83. ^{1}H NMR (300 MHz, C_6D_6, 300 K) δ (ppm) = 3.13 (m), 2.61 (m) 2.40 (m) (6H, –CH=CH$_2$); 1.38(m), 1.20(s), 1.18(s) (63H, *iso*-Pr); 0.62 (s, 6H, SiMe$_2$); 0.02 (s, 6H, SiMe$_2$). ^{13}C NMR (75.42 MHz, C_6D_6, 300 K) δ (ppm) = 49.24 (s) (d, $J_{\text{C–Pt}}$ = 168.13 Hz) 49.14 (d, $J_{\text{C–Pt}}$ = 168.13 Hz); 44.39 (s) (d, $J_{\text{C–Pt}}$ = 107.08 Hz); 44.16 (s) (d, $J_{\text{C–Pt}}$ = 107.38 Hz) 18.68 (–Me); 14.57 (–CH(Me)$_2$); 2.15, −1.41 (SiMe$_2$). ^{31}P NMR (121.47 MHz, C_6D_6, 300 K) δ (ppm) = 86.40 ($J_{\text{P–Pt}}$ = 6379.05 Hz).

*2.2.9.3. Complex [Pt{η^4-(H$_2$C=CHSiMe$_2$)$_2$O}{P(OSiMePh$_2$)$_3$}] (**9**).* Yield 0.75 g (98%). Anal. calc. for $C_{47}H_{57}O_4PPtSi_5$ C 53.64; H 5.46; found C 53.70; H 5.72. ^{1}H NMR (300 MHz, C_6D_6, 300 K) δ (ppm) = 7.58 (m), 7.37 (m) (30H, *o*,*m*,*p*-Ph); 2.80–3.80 (m) (6H, –CH=CH$_2$); 0.62 (s, 9H, –SiPh$_2$Me); 0.43, 0.42 (s) (6H, –Me); −0.23, −0.35 (6H, –Me). ^{31}P NMR (121.47 MHz, C_6D_6, 300 K) δ (ppm) = 97.04 ($J_{\text{P–Pt}}$ = 6332.6 Hz).

Table 2
Selected geometrical parameters (distances in Å and angles in°). X describes the middlepoint of the double bond.

	10	**11**
Pt–P	2.2.2405(8)	2.2444(13)
Pt–X	2.034(3) 2.043(3)	2.033(4) 2.040(3)
P–O	1.581(2) 1.584(2) 1.585(2)	1.564(3) 1.583(3) 1.592(3)
O–Si	1.655(2) 1.656(2) 1.660(2)	1.632(3) 1.607(3) 1.633(3)
⟨Si–O(^{t}Bu)⟩		1.604(9)
⟨Si–C(ar)⟩	1.865(5)	
X–Pt–X	133.01(13)	131.4(2)
X–Pt–P	113.54(10) 113.45(9)	114.21(12) 114.28(16)

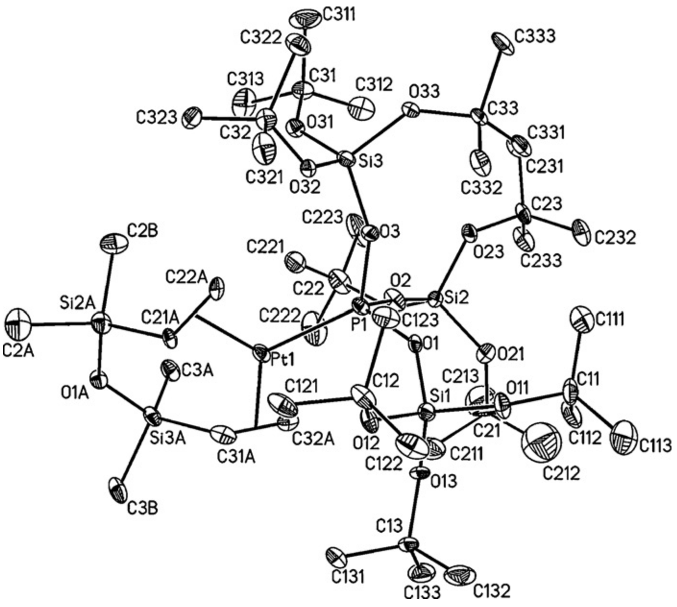


Fig. 2. Anisotropic ellipsoid representation of complex **11**. The ellipsoids are drawn at 50% probability level, hydrogen atoms are omitted for clarity.

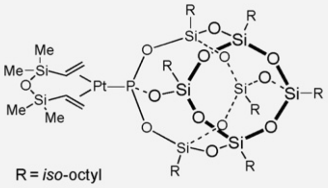
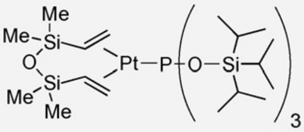
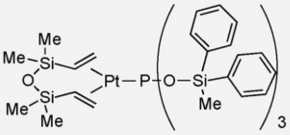
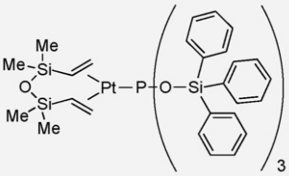
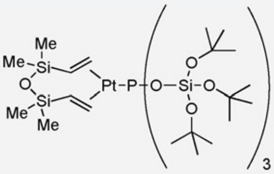
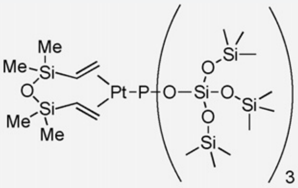
*2.2.9.4. Synthesis of complex [Pt{η^4-(H$_2$C=CHSiMe$_2$)$_2$O}{P(OSiPh$_3$)$_3$}] (**10**).* 15 mL of benzene was added to a Schlenk's tube containing 1.0 g (1.17 mmol) of compound **4**. The resulting mixture was warmed up to 50 °C to dissolve the phosphite. Subsequently, 7.48 g (1.15 mmol of Pt) solution of Karstedt's catalyst (3% of Pt in xylene) was added dropwise to the reaction mixture. The reaction was conducted for 24 h at 50 °C on stirring the reaction mixture with a magnetic stirrer. After this time solvent was evaporated and the solid obtained was dried under vacuum. Crude complex was washed three times with 5 mL of pentane and dried under vacuum. Yield 1.35 g (95%).

Anal. calc. for $C_{62}H_{63}O_4PPtSi_5$ C 60.12; H 5.13; found C 60.17; H 5.18. ^{1}H NMR (300 MHz, C_6D_6, 300 K) δ (ppm) = 7.60 (d), 7.18 (t), 7.06 (t) (45H, *o*,*m*,*p*-Ph); 2.43 (m), 2.25(m) (6H, –CH=CH$_2$); 0.473 (s), 0.471 (s) (6H, –Me); −0.09 (6H, –Me). ^{13}C NMR (75.42 MHz, C_6D_6, 300 K) δ (ppm) = 136.18; 133.93; 130.45; 130.88; 128.13; 50.60 (d, $J_{\text{C–Pt}}$ = 6.6 Hz); 46.14 (d, $J_{\text{C–Pt}}$ = 17.58 Hz); 1.99, 1.95, −0.83. ^{31}P NMR (121.47 MHz, C_6D_6, 300 K) δ (ppm) = 94.25 ($J_{\text{P–Pt}}$ = 6454.55 Hz).

*2.2.9.5. Complex [Pt{η^4-(H$_2$C=CHSiMe$_2$)$_2$O}{P(OSi(O^{t}Bu$_3$)$_3$}] (**11**).* Crude complex was washed three times with 3 mL of pentane at minus 70 °C, and dried under vacuum. Yield 1.40 g (97%). Anal. calc. for $C_{44}H_{99}O_{13}PPtSi_5$ C 43.94; H 8.30; found C 43.99; H 8.36. ^{1}H NMR (300 MHz, C_6D_6, 300 K) δ (ppm) = 3.26 (m), 2.64 (m), 1.89 (m) (6H, –CH=CH$_2$); 1.35 (s), 1.34 (s), 1.32 (s), 1.31 (s), 1.28 (s), 1.27 (s) (81H, –O^{t}Bu); 0.313 (s), 0.310 (s) (6H, –Me); −0.26 (6H, –Me). ^{13}C NMR (75.42 MHz, C_6D_6, 300 K) δ (ppm) = 73.72; 48.62 (td, J = 73.0 Hz, J = 6.2 Hz); 42.98; (td, J = 56.2 Hz, J = 17.6 Hz); 31.85; 31.33; 1.76; 1.74; −1.05. ^{31}P NMR (121.47 MHz, C_6D_6, 300 K) δ (ppm) = 81.74 ($J_{\text{P–Pt}}$ = 6521.42 Hz).

*2.2.9.6. Complex [Pt{η^4-(H$_2$C=CHSiMe$_2$)$_2$O}{P(OSi(OSiMe$_3$)$_3$)$_3$}] (**12**).* Yield 1.34 g (98%). Anal. calc. for $C_{35}H_{99}O_{13}PPtSi_{14}$ C 31.20; H 7.41; found C 31.27; H 7.46. ^{1}H NMR (300 MHz, C_6D_6, 300 K) δ (ppm) = 3.33 (m), 2.84 (m), 2.54 (m) (6H, –CH=CH$_2$); 0.62 (s, 6H, SiMe$_2$), 0.31 (s, 81H, –SiMe$_3$); 0.14 (s, 6H, SiMe$_2$). ^{13}C NMR

Table 3
Catalytic properties of the new platinum(0) complexes in cross-linking of the model mixture of vinyl-terminated polydimethylsiloxane and polyhydromethylsiloxane in the presence of [Pt] = 10^{-5} mol.

Catalysts		Pot-life at 25 °C	Curing time at 120 °C	DSC analysis	
				Average peak temperature (°C)	Average enthalpy of reaction (J/g)
Pt/DAM				111.7	−20.35
7		12 h	1 min 30 s	96.6	−8.89
8		30 days (no curing)	3 min	164.5	−21.93
9		30 min	Not measured	105.6	−5.16
10		40 days (no curing)	2 min	124.4	−22.50
11		30 days (no curing)	2 min	133.65	−20.58
12		30 days (no curing)	5 min	105.2	−21.48

Reaction conditions (DSC): [HSi]:[Pt] = 1:10^{-5}, temperature rate—10 °C/min, helium.

(75.42 MHz, C_6D_6, 300 K) δ (ppm) = 48.67 (s) (d, J_{C-Pt} = 168.43 Hz), 48.58(s) (d, J_{C-Pt} = 168.38 Hz); 44.72 (s) (d, J_{C-Pt} = 111.30 Hz); 44.49 (d, J_{C-Pt} = 110.85 Hz); 2.70 (–$SiMe_3$); 2.07, 2.00; 1.67, 1.63 ($SiMe_2$). ^{31}P NMR (121.47 MHz, C_6D_6, 300 K) δ (ppm) = 87.21 (J_{P-Pt} = 6415.73 Hz).

2.3. General procedure of curing time and pot-life determination

The calculated amounts a well-defined Pt complex were added to 4.00 g mixture of vinyl-terminated polydimethylsiloxane and polyhydromethylsiloxane. The catalyzed mixture was stirred for 30 min. The curing process of the polysiloxanes mixture was performed in an aluminum vessel (15 mm × 20 mm × 7 mm) using a hot plate heated up to 120 °C. The curing time was measured from the moment of placing the aluminum vessel with liquid reaction mixture on the hot plate until getting the dry cured material.

The pot-life time was measured from the moment of Pt-catalyst addition to mixture of mentioned above polysiloxanes up to the total curing of the initial mixture at room temperature. Typically, the pot-life is defined as the time when a viscosity of the catalyzed mixture is doubled.

3. Results and discussion

As we discussed previously [24f–h], the key step of Karstedt's catalyst inhibition process is the Pt–P bond formation by coordination of phosphites ligand, which leads to the formation of a new complex. The complex formed is responsible for a change of Pt catalytic activity in cross-linking of polysiloxane

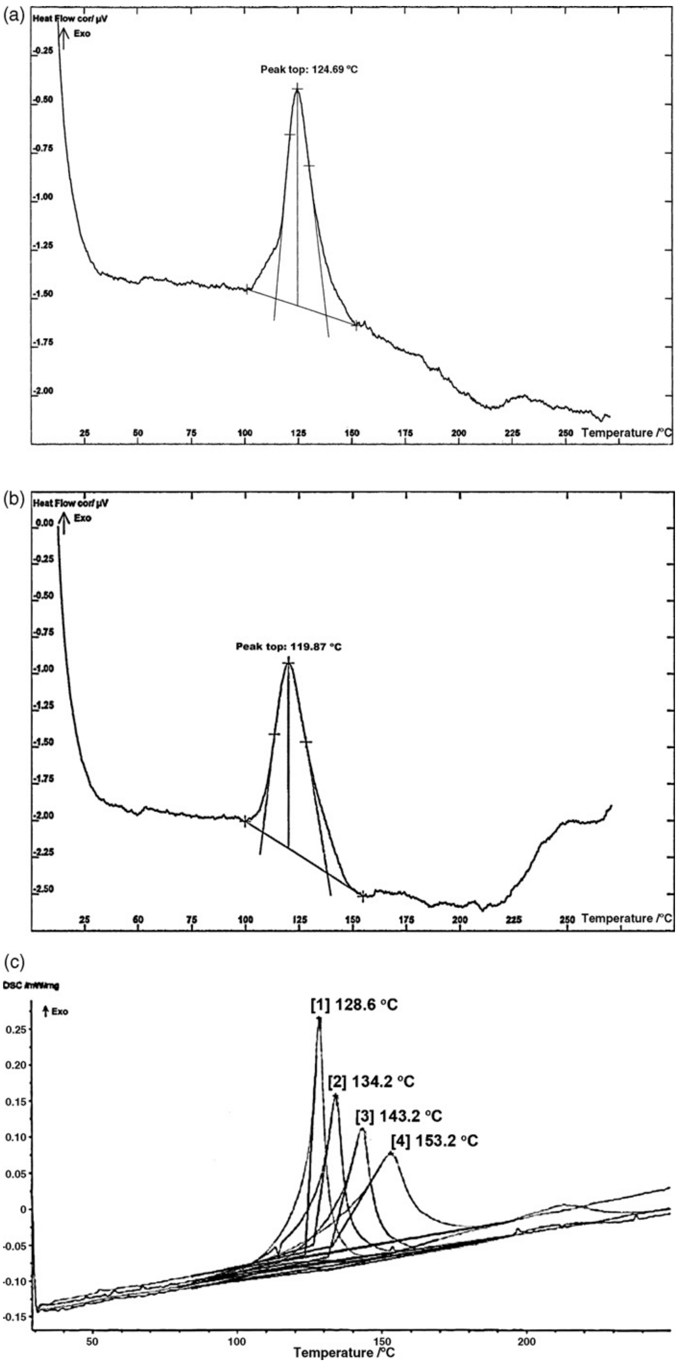


Fig. 3. DSC curves of the curing process: (a) catalyzed by 10 ppm of the complex **10**; (b) catalyzed by 10 ppm of the complex **10**—after 10 days of storage; (c) catalyzed by Karstedt's/DAM catalytic system (curves [1]—100 ppm of Pt, [2]—70 ppm of Pt, [3]—50 ppm of Pt, [4]—25 ppm of Pt)

fluids by hydrosilylation. We also concluded that separately synthesized, well-defined complexes of Pt with organophosphites might be employed as effective catalysts of the cross-linking process, since their catalytic activity at room temperature is very low; consequently we developed the one-part polysiloxane compound with relatively long storage time. Results presented in the above-mentioned publication showed that it is possible to adjust catalytic activity of platinum centre in hydrosilylation reaction by controlling bulkiness and electronic properties of the substituents at phosphorous center [24h]. Unexpected result obtained for $P(OC_6F_5)_3$ encouraged us to look for an explanation of such phenomenon. It is commonly known that reactivity of a metal centre depends on the electronic properties as well as on the steric hindrance of coordinated ligands. The hindrance effect is produced by the size of substituents bonded to the donating atom, but σ-donation properties as well as back-bonding interaction of this atom depend strongly on electronic properties of the substituents. The influence of electronic properties of phosphorus ligands on the metal centre was widely discussed in textbooks [33]. We have chosen the values of chemical shift in ^{31}P NMR spectra as benchmark measure of the phosphite electronic properties. The data collected for organosubstitued phosphites show that the ^{31}P NMR chemical shifts are in the range of 127–148 ppm for aryl derivatives and 137–145 ppm for aliphatic derivatives [24h]. The phosphites studied, whose chemical shifts were nearly 130 ppm for arylphosphites and 140 ppm for alkylphosphites, appeared convenient ligands controlling platinum catalytic activity in the curing process. The analysis of NMR data encouraged us to look for other phosphites with bulky substituents and having low values of ^{31}P NMR chemical shift. Reported by Feher phosphorosilsesquioxanes [34] well satisfy the above requirements (^{31}P NMR chemical shift of the phosphorus nuclei at 86.12 ppm, sufficiently large Tolman's cone angle of 167°, which is similar to PPh_3). Phosphorus-*iso*-octylsilsesquioxane (**1**) was synthesized according to the method proposed in [24f–h]. We have looked also for other silicon containing phosphites, cheapest and easier to produce, which could be used as efficient inhibitors of Karstedt's catalyst or ligands of new Pt complexes. Previously reported method for the synthesis of tris(triorganosilyl)phosphites involve use of triorganochlorosilane as a substrate, which leads to formation of undesirable and difficult to remove by-products. To eliminate this problem, we have used for the first time sodium silanolates for the preparation of various tris(triorganosilyl)phosphites. Proceeding according to the new method presented in [24f–h] and using simple silanols instead of POSS-*iso*-octylsilsesquioxanes, new silylphosphites (**2**–**6**) were synthesized, and well characterized by NMR method [35]. We affirmed that ^{31}P NMR chemical shifts values for phosphorus atom surrounded by organosilicon substituents were in the expected range of 109–112.5 ppm for compounds **2**, **4**–**6**. Interestingly, the ^{31}P NMR chemical shift for compound **3** had exceptionally low value of −13.61 ppm. In the next step all the compounds obtained were employed for the preparation of new Karstedt's based platinum complexes (**7**–**12**) [35], according to the procedures described previously [24f–h]. The new platinum compounds obtained were fully characterized by NMR technique as well as structures of **10** and **11** were determined by X-ray analysis.

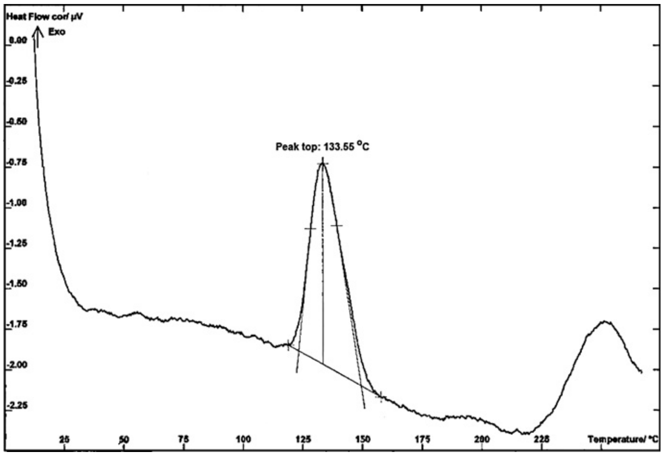


Fig. 4. DSC curve of the curing process performed in the presence of 10 ppm of complex **11**.

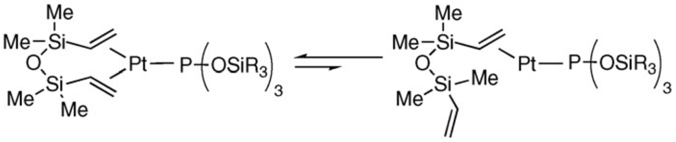
Figs. 1 and 2 show the perspective views of complexes **10** and **11**; Table 2 presents some selected geometrical parameters. The coordination of Pt is triangular; the Pt atom is displaced from the plane made by three points: P1 atom and the middlepoints of the double bonds (X1 and X2) only by 0.002(1) Å in **10**. However, for **11** this displacement is more significant, 0.054(3) Å. The distances Pt–X and Pt–P take typical mean values of 2.040 and 2.242 Å, respectively. The conformation of six-membered organometallic ring Pt–X–Si–O–Si–X might be described as flattened, distorted chair. In both complexes, the 1,3-divinyltetramethyldisiloxane fragment has approximate C_s symmetry, with the mirror plane passing through the oxygen atom. The four carbon atom of two vinyl groups are in a good approximation planar, and the platinum atom in both cases lies almost exactly in the plane which makes small dihedral angle of 2–3° with the coordination plane. It might be noted that (P)–O–Si distances in **10**, where Si is further connected with phenyl rings are significantly longer than in **11**, where there are *tert*-butoxy groups. The largest flexibility is observed in P–O–Si angles (changes as large as 30°). The crystal packing is determined mainly by close packing requirement and van der Waals interactions.

The catalytic properties of the new platinum complexes were examined in a cross-linking of the model mixture of vinyl-terminated polydimethylsiloxane and polyhydromethylsiloxane. Results, which include a pot-life at 25 °C, curing time at 120 °C as well as DSC analysis, are compiled in Table 3.

The complexes obtained appear efficient and very promising catalysts for vinyl-terminated polydimethylsiloxane cross-linking process. Particularly exciting results were obtained for complexes **8**, **10**–**12**. These complexes showed very low catalytic activity at room temperature (the catalyzed polysiloxane formulation did not show any symptoms of cure for at least 40 days), provided relatively short curing time at 120 °C, as well as average value of enthalpy (J/g) and average peak temperature were approximately similar to those obtained for the commercial Pt/DAM catalytic system (Table 3).

Exemplary DSC curves (Figs. 3a and 4) recorded for the curing process performed in the presence of 10 ppm catalysts **10** and **11** show that the cross-linking process occurs at lower temperature than the reaction catalyzed by 25 ppm of Pt(0) as Karstedt's catalyst with DAM as inhibitor (Fig. 3c). The DSC curves of the cross-linking process in the presence of the new complexes **10** and **11** showed sharper exothermal cure peaks, than that one recorded for the process catalyzed by 25 ppm of Pt(0)-Karstedt's/DAM. These peaks were comparable to the cure peak recorded at 100 ppm of Pt(0)-Karstedt's/DAM (Fig. 3c).; therefore the new complexes appeared more efficient then the commercially used Karstedt's/DAM catalytic system. It is also essential that the new complexes are stable as formulated into the polysiloxane mixture and their catalytic activity is not affected by a long storage time. Curing tests showed that the activity of complex **10** added to polysiloxanes mixture does not change after **10** days of storage time. This result was additionally confirmed by DSC measurement (Fig. 3a and b), which showed that average peak temperature as well as the average enthalpy of cross-linking process for polysiloxane system catalyzed by **10** did not change after 10 days of storage.

The above results suggest that introduction of phosphites with bulky organosilicon substituents into platinum coordination sphere makes the metal centre less accessible to organosilicon polymeric reactants at room temperature. Additionally, more electron-donating character of the triorganosilicon phosphites ligands in comparison with that of organosubstituted phosphites might stabilize a six-membered organometallic ring Pt–X–Si–O–Si–X (Scheme 1) by increasing of back-bonding interaction between the platinum centre and vinyl groups of 1,3-divinyltetramethyldisiloxane ligand. As a consequence, the equilibrium between both forms of the complex can be shifted to the left side of the equation; therefore the new complexes are inactive at storage conditions and provide a long pot-life for catalyzed silicone.



Scheme 1.

On the other hand, relatively short pot-life observed for the silicone formulations catalyzed by complexes **7** and **9** as well as low enthalpy of the curing process might be explained, by not enough bulky ligands coordinated to the platinum centre leading in consequence to hydrosilylation reaction at room temperature.

4. Conclusions

Various tris(triorganosilyl)phosphites with bulky silyl substituents were synthesized and used as efficient ligands coordinated to the platinum centre. New, well-defined Pt(0)-(DVTMDS)-tris(triorganosilyl)phosphites complexes (**7**–**12**) were synthesized and characterized by NMR spectroscopy (X-ray structure of complexes **10** and **11** were also solved). The curing studies of the model polysiloxane formulation proved that new platinum(0) complexes (**8**, **10**–**12**) showed a very low catalytic activity at room temperature giving sufficiently long pot-life for the catalyzed silicone (up to 40 days) and efficiently catalyze silicone cross-linking process at elevated temperature. The high catalytic activity of the now complexes was confirmed by the model system curing studies and DSC method. The selected complexes are promising candidates as novel Pt(0) catalysts for commercial one-part silicone formulations.

Acknowledgment

The financial support from Momentive Performance Materials (formerly GE Silicones) is gratefully acknowledged.

References

[1] L. Wozniak, J. Chojnowski, Tetrahedron 45 (1986) 2465–2524.
[2] (a) S.N. Borisov, M.S. Voronkov, E.J. Lukevits, Kremneorganicheskye Proizvodnye Fosfora i Seryizd. Khimya, Moskva 1968 (in Russian), English ed. Organosilicon Derivatives of Phosphorus and Sulfur. Plenum Press, New York (1971);
(b) E.A. Chernyshev, E.F. Bugerenko, Organometal. Chem. Rev. Sect. A 3 (1968) 469–478.
[3] (a) T. Hata, M. Sekine, in: W.J. Stec (Ed.), Phosphorus Chemistry Directed towards Biology, Pergamon Press, Oxford, 1980, p. 187;
(b) T. Hata, M. Sekine, J. Synth. Org. Chem. Jpn. 39 (1981) 918–922 (in Jap.).
[4] N.F. Orlov, E.V. Sudakova, Zh. Obshch. Khim. 39 (1969) 222–225.
[5] E.F. Bugerenko, E.A. Chernyshev, E.M. Popov, Izv. Akad. Nauk SSSR, Ser. Khim. (1986) 1391.
[6] J. Chojnowski, M. Cypryk, J. Michalski, L. Wozniak, R. Corriu, G. Lanneau, Tetrahedron 42 (1986) 385–397.
[7] (a) B. Marciniec, J. Guliński, W. Urbaniak, Z.W. Kornetka, in: B. Marciniec (Ed.), Comprehensive Handbook on Organosilicon Chemistry, Pergamon, Oxford, 1992, pp. 758;
(b) B. Marciniec, H. Maciejewski, C. Pietraszuk, P. Pawluć, in: B. Marciniec (Ed.), Hydrosilylation—A Comprehensive Review on Recent Advances, Springer, 2009, p. 408.
[8] T. Hata, M. Sekine, N. Kagawa, Chem. Lett. (1975) 635–636.
[9] A.F. Rosenthal, A. Grignauz, L.A. Vargas, J. Chem. Soc. Chem. Commun. (1976) 384–385.
[10] M.G. Voronkov, Yu.I. Skorik, Zh. Obshch. Khim. 35 (1965) 106–110.
[11] M. Sekine, K. Okimoto, K. Yamada, T. Hata, J. Org. Chem. 46 (1981) 2097–2107.
[12] A.F. Rosenthal, L.A. Vargas, Y.A. Isaacson, R. Bittman, Tetrahedron Lett. (1975) 977–980.
[13] R.-M. Schoth, E. Lork, F.U. Seifert, E. Breuer, G.-V. Roschenthaler, Chem. Ber. Recueil. 130 (1997) 279–281.
[14] (a) J. Zoń, Pol. J. Chem. 55 (1981) 643–646;
(b) A.P. Avdeenko, V.P. Ryazantsev, A.I. Mishchenko, Zh. Obshch. Khim. 56 (1986) 2491–2494.
[15] N.F. Orlov, B.L. Kaufman, Zh. Obshch. Khim. 38 (1968) 1842–1845.
[16] N.F. Orlov, M.A. Belokrinitskii, O.N. Dolgov, B.L. Kaufman, L.N. Slesar, M.S. Sorokin, E.V. Sudakova, Khim. Primen. Fosfoorg. Soedin. (Tr. Konf. Fourth 1969) Nauka, Moscow, 1972, p. 396.

[17] M. Sekine, Y. Yamamoto, A. Hashizume, T. Hata, Chem. Lett. (1977) 485–488.
[18] E.E. Nifantyev, T.S. Kukhareva, T.N. Popkova, O.V. Davybochkina, Zh. Obshch. Khim. 56 (1986) 304–309.
[19] T.N. Popkova, T.S. Kukhareva, A.R. Bekker, E.E. Nifantyev, Zh. Obshch. Khim. 56 (1986) 1813–1815.
[20] L.N. Lewis, J. Stein, Y. Gao, J. Dong, J. Organomet. Chem. 521 (1996) 221–227.
[21] L.N. Lewis, J. Stein, Y. Gao, R.E. Colborn, G. Hutchins, Platinum Metals Rev. 41 (1997) 66–75.
[22] F. Faglioni, M. Blanco, W.A. Goddard, D. Saunders, J. Phys. Chem. B 106 (2002) 1714–1721.
[23] (a) R.P. Eckberg, US Patent 4,256,870 (1981);
(b) R.P. Eckberg, US Patent 4,340,647 (1982);
(c) M.E. Grenoble, R.P. Eckberg, US Patent 4,448,815 (1984);
(d) R.P. Eckberg, US Patent 4,476,166 (1984);
(e) K.C. Melancon, US Patent 4,533,575 (1985);
(f) K.C. Melancon, US Patent 4,504,645 (1985);
(g) P.Y.K. Lo, L.E. Thayer, A.P. Wright, US Patent 4,562,096 (1985);
(h) P.Y.K. Lo, US Patent 4,774,111 (1988);
(i) P.Y.K. Lo, LR.E. Thayer, A.P. Wright, US Patent 4,783,552 (1988);
(j) K. Chung, A.P. Wrigth, M-H. Yea, US Patent 5,036,117 (1991).
[24] (a) G.H. Munster & CO., GB Patent 1054658 (1967);
(b) A.J. Chalk, N.Y. Scotia, US Patent 3,188,300 (1965);
(c) L.N. Lewis, US Patent 4,645,815 (1987);
(d) M. Ikeno, M. Tanaka, K. Sato, US Patent Application Publication 2004/0116561;
(e) M. Tanaka, K. Sato, M. Ikeno, US Patent Application Publication 2006/0047097;
(f) H. Steinberger, B. Marciniec, I. Kownacki, International Publication Number WO 2010/009755 A1 (2010);
(g) H. Steinberger, B. Marciniec, I. Kownacki, International Publication Number WO 2010/009752 A1 (2010);
(h) I. Kownacki, B. Marciniec, H. Steinberger, M. Kubicki, M. Hoffman, A. Ziarko, K. Szubert, M. Majchrzak, S. Rubinsztajn, Appl. Catal. A: Gen. 362 (2009) 106–114;
(i) M.E. Lutz, B.T. Nguyen, R.K. King, US Patent 5,380,812 (1995).
[25] (a) M. Hatanaka, M. Matsumoto, M. Yonezawa US Patent 4,157,426 (1979);
(b) M. Hatanaka, S. Nagashima US Patent 4,256,616 (1981).
[26] P.B. Hitchcock, M.F. Lappert, C. MacBeath, F.P.E. Scott, N.J.W. Warhurst, J. Organomet. Chem. 528 (1997) 185–190.
[27] J. Liedtke, S. Loss, G. Alcaraz, V. Gramlich, H. Grutzmacher, Angew. Chem. Int. Ed. 38 (1999) 1623–1626.
[28] S. Liedtke, C. Loss, H. Widauer, Grutzmacher, Tetrahedron 56 (2000) 143–156.
[29] Oxford Diffraction. CrysAlisCCD, User Guide v.171. Oxford Diffraction Poland Sp., Wrocław, Poland, 2003.
[30] Oxford Diffraction. CrysAlisRed, CCD data reduction GUI v.171. Oxford Diffraction Poland Sp., Wrocław, Poland, 2003.
[31] G.M. Sheldrick, Acta Crystallogr. A46 (1990) 467–473.
[32] G.M. Sheldrick. SHELXL-97, Program for the Refinement of Crystal Structures, University of Gőttingen, Gőttingen, Germany, 1997.
[33] C. Elschenbroich, A. Salzer, Organometallics. A Concise Introduction, 2nd ed., VCH, Weinheim, 1992, p. 495.
[34] J.F. Feher, T. Budzichowski, Organometallics 10 (1991) 812–815.
[35] H. Steinberger, B. Marciniec, I. Kownacki, International Publication Number WO 2010/009754 A1 (2010).