

PREPARATION OF ORGANOMETALLIC AND SILYL COMPLEXES OF PALLADIUM(II) VIA $[\text{PdCl}(\text{SnCl}_3)_2\text{L}_2]$, WHERE $\text{L} = \text{PPh}_3, \text{P}(p\text{-Tol})_3$ Małgorzata NOSKOWSKA¹ and Wojciech DUCZMAL^{2,*}*Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland;
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A new method for preparing organometallic and monosilyl complexes of Pd(II), based on the interaction between $[\text{PdCl}(\text{SnCl}_3)_2\text{L}_2]$ ($\text{L} = \text{PPh}_3$ or $\text{P}(p\text{-Tol})_3$) and appropriate organohalogen compound or chlorosilane has been developed. The products without tin have been obtained with good yield (85–97%). The reaction mechanism has been proposed on the basis of kinetic and chemometric investigations of the reaction between $[\text{PdCl}(\text{SnCl}_3)(\text{PPh}_3)_2]$ and Me_2SiCl_2 .

Keywords: Palladium; Tin; Synthetic methods; Kinetics; Trichlorostannate; Organometallic complexes; Silyl complexes; Phosphine complexes.

The complexes of palladium(II) have gained enormous interest in the last decades because of their catalytic activity, e.g. in the homogenous olefin polymerisation¹, oxidation of olefins to aldehydes and ketones² or Heck reaction³. The usual way of preparing these complexes is via addition of ligands to metal halides⁴. Compounds containing the M–C bond are usually prepared by reactions with Grignard or organolithium reagents⁵, oxidative addition⁶, elimination and metathesis⁷.

Silyl complexes of palladium(II) are important intermediates of many reactions with silicon compounds, such as hydrosilylation, bis-silylation and synthesis of enynes by the coupling of Me_3SiI , acetylenes and acetylenic tin reagents⁸. They are rather unstable and there are only a few examples of their successful isolation. Majority of silyl palladium complexes are bis-silyl compounds, which are obtained by oxidative addition of hydrosilanes or disilanes to phosphine complexes of palladium^{9,10}. Only a few reports on the synthesis of monosilane complexes of palladium have been published¹¹; however, their formation is often proposed to explain the mechanistic aspects of many processes catalyzed by palladium compounds.

Working with trichlorostannate complexes of palladium(II), we have found that they can easily react with MeI , PhBr , PhCH_2Cl or Me_2SiCl_2 . The

reactions lead to the formation of complexes of palladium(II) without tin and on this basis we have developed a new, simple method of preparation of organometallic and monosilyl complexes of palladium(II) via $[\text{PdCl}(\text{SnCl}_3)\text{L}_2]$.

EXPERIMENTAL

All manipulations were performed under an argon atmosphere using conventional Schlenk techniques. NMR analyses (δ , ppm) were performed on a Varian Gemini 300 spectrometer for CDCl_3 solutions. ^1H NMR spectra were referenced internally using the residual protons in the deuterated solvent and reported relative to tetramethylsilane. ^{31}P NMR spectra were also recorded on a Varian Gemini 300 spectrometer. UV/VIS spectra were recorded on a Specord UV/VIS spectrophotometer (Carl Zeiss, Jena). IR spectra (ν , cm^{-1}) were measured on an FT-IR Raman Magna 760 Nicolet instrument with KBr disks or Nujol nulls. Elemental analyses were performed on a Euro-Vector EA 3000. Pd was determined by spectrophotometric iodide method¹².

Starting Materials

$[\text{PdCl}(\text{SnCl}_3)(\text{PPh}_3)_2]$ and $[\text{PdCl}(\text{SnCl}_3)\{\text{P}(p\text{-Tol}_3)\}_2]$ were prepared according to a previously described procedure¹³. Purification of benzene (POCh Poland), bromobenzene (Fluka), benzyl chloride (POCh Poland) and methyl iodide (POCh Poland) involved refluxing with appropriate drying agent and distillation under argon. Petroleum ether (POCh Poland) and Me_2SiCl_2 (Fluka) were purified by distillation in argon atmosphere.

Reaction of PhBr, PhCH_2Cl or Me_2SiCl_2 with $[\text{PdCl}(\text{SnCl}_3)\text{L}_2]$

$[\text{PdCl}(\text{SnCl}_3)\text{L}_2]$ (0.1 mmol) and an appropriate reagent (PhBr, PhCH_2Cl , Me_2SiCl_2) (0.12 mmol) were placed in a screw-cap vial, flushed with argon. The mixture was well shaken and heated at 80 °C for 24 h to ensure complete conversion. After this time the vial was opened and the reaction mixture was filtered. The precipitated solid was washed with petroleum ether several times and left in the air to dry.

$[\text{PdBr}(\text{Ph})(\text{PPh}_3)_2]$. ^1H NMR (CDCl_3): 6.25 (t, 2 H); 6.39 (t, 1 H); 6.66 (d, 2 H); 7.28 (m, 18 H); 7.52 (m, 12 H). ^{31}P NMR (CDCl_3): 23.5 (s). IR (KBr): 3075, 3055, 3005, 1562, 1432, 1057, 1025, 1015 ($\nu(\text{Pd-Ph})$). For $\text{C}_{42}\text{H}_{35}\text{BrP}_2\text{Pd}$ (787.3) calculated: 64.01% C, 4.47% H, 13.50% Pd; found: 63.98% C, 4.50% H, 13.52% Pd.

$[\text{PdCl}(\text{PhCH}_2)(\text{PPh}_3)_2]$. ^1H NMR (CDCl_3): 5.2 (m, 2 H); 6.03–6.71 (m, 5 H); 7.26 (m, 18 H); 7.52 (m, 12 H). ^{31}P NMR (CDCl_3): 28.72 (s). IR (Nujol): 361 ($\nu(\text{Pd-Cl})$). For $\text{C}_{43}\text{H}_{37}\text{ClP}_2\text{Pd}$ (755.1) calculated: 68.14% C, 4.92% H, 14.07% Pd; found: 67.89% C, 4.81% H, 14.12% Pd.

$[\text{PdCl}(\text{SiMe}_2\text{Cl})(\text{PPh}_3)_2]$. ^1H NMR (CDCl_3): 0.39 (s, 6 H); 7.26–7.37 (m, 18 H); 7.48–7.54 (m, 12 H). The solubility of $[\text{PdCl}(\text{SiMe}_2\text{Cl})(\text{PPh}_3)_2]$ in CDCl_3 is too low for ^{31}P NMR measurement. IR (Nujol): 1261, 820 ($\nu(\text{Si-Me})$); 431 ($\nu(\text{Si-Cl})$); 348 ($\nu(\text{Pd-Cl})$). For $\text{C}_{38}\text{H}_{36}\text{Cl}_2\text{P}_2\text{SiPd}$ (757.6) calculated: 59.89% C, 4.55% H, 13.96% Pd; found: 60.04% C, 4.77% H, 14.00% Pd.

$[\text{PdBr}(\text{Ph})\{\text{P}(p\text{-Tol}_3)\}_2]$. ^1H NMR (CDCl_3): 1.85 (s, 18 H); 6.25 (t, 2 H); 6.39 (t, 1 H); 6.66 (d, 2 H); 7.26–7.31 (m, 12 H); 7.40–7.58 (m, 12 H). ^{31}P NMR (CDCl_3): 24.3 (s). IR (KBr): 3073,

3048, 3007, 1558, 1426, 1047, 1025, 1019 ($\nu(\text{Pd}-\text{Ph})$). For $\text{C}_{48}\text{H}_{47}\text{BrP}_2\text{Pd}$ (869.5) calculated: 66.07% C, 5.43% H, 12.24% Pd; found: 66.48% C, 5.35% H, 12.20% Pd.

$[\text{PdCl}(\text{PhCH}_2)\{\text{P}(p\text{-Tol})_3\}_2]$. ^1H NMR (CDCl_3): 2.29 (s, 18 H); 5.2 (m, 2 H); 7.01 (m, 15 H); 7.50 (m, 14 H). ^{31}P NMR (CDCl_3): 27.6 (s). IR (Nujol): 362 ($\nu(\text{Pd}-\text{Cl})$). For $\text{C}_{48}\text{H}_{34}\text{ClP}_2\text{Pd}$ (812.1) calculated: 69.89% C, 5.86% H, 12.67% Pd; found: 69.72% C, 5.62% H, 12.69% Pd.

$[\text{PdCl}(\text{SiMe}_2\text{Cl})\{\text{P}(p\text{-Tol})_3\}_2]$. ^1H NMR (CDCl_3): 0.28 (s, 6 H); 2.25 (s, 18 H); 7.28–7.30 (m, 12 H); 7.51–7.56 (m, 12 H). The solubility of $[\text{PdCl}(\text{SiMe}_2\text{Cl})\{\text{P}(p\text{-Tol})_3\}_2]$ in CDCl_3 is too low for ^{31}P NMR measurement. IR (Nujol): 1261, 804 ($\nu(\text{Si}-\text{Me})$); 446 ($\nu(\text{Si}-\text{Cl})$); 352 ($\nu(\text{Pd}-\text{Cl})$). For $\text{C}_{44}\text{H}_{48}\text{Cl}_2\text{SiP}_2\text{Pd}$ (841.6) calculated: 62.57% C, 5.72% H, 12.63% Pd; found: 62.69% C, 5.63% H, 12.58% Pd.

Reaction of MeI with $[\text{PdCl}(\text{SnCl}_3)\text{L}_2]$

Methyl iodide (0.12 mmol) was added to a solution of $[\text{PdCl}(\text{SnCl}_3)\text{L}_2]$ (0.1 mmol) in benzene at 25 °C under argon. The resulting mixture was stirred at 25 °C for 2 h and petroleum ether (40 ml) was then added. The yellow precipitate was collected by filtration and left in air for drying.

$[\text{PdI}(\text{Me})(\text{PPh}_3)_2]$. ^1H NMR (CDCl_3): 0.27 (t, 3 H); 7.26–7.33 (m, 18 H); 7.52–7.69 (m, 12 H). IR (KBr): 2980, 2910 ($\nu(\text{C}-\text{H})$). For $\text{C}_{37}\text{H}_{33}\text{IP}_2\text{Pd}$ (770.5) calculated: 57.50% C, 4.30% H, 13.77% Pd; found: 57.49% C, 4.36% H, 13.80% Pd.

$[\text{PdI}(\text{Me})\{\text{P}(p\text{-Tol})_3\}_2]$. ^1H NMR (CDCl_3): 0.27 (t, 3 H); 1.88 (s, 18 H); 7.26–7.33 (m, 12 H); 7.52–7.69 (m, 12 H). ^{31}P NMR (CDCl_3): 37.16 (s). IR (Nujol): 2978, 2862 ($\nu(\text{C}-\text{H})$); 259 ($\nu(\text{Pd}-\text{I})$). For $\text{C}_{43}\text{H}_{37}\text{ClP}_2\text{Pd}$ (755.1) calculated: 60.23% C, 5.29% H, 12.44% Pd; found: 61.05% C, 5.17% H, 12.38% Pd.

Kinetic Studies

Standard solutions of the complex and chlorosilanes were prepared by dissolving weighed or pipetted portions of reagents in chloroform. For kinetic experiments, the required aliquots of these solutions were transferred to silica cells (10 mm thick), equipped with a Rotaflo stopcock and mixed. The progress of the reaction were followed spectrophotometrically at 25 °C by repeated scanning of the at suitable times. At least a ten-fold excess of chlorosilane over the complex ensured the pseudo-first order kinetics in all runs¹⁴ and prevented spontaneous decomposition of Pd complex in chloroform solutions. The obtained sets of spectrophotometrical data were subjected to factor analysis in order to determine the number and spectral characteristics of abstract colour components in the systems under study (principal component analysis, PCA). The spectral and concentration characteristics of the real independent colour components present in the system were obtained from target factor analysis¹⁵. Evaluation of the applied kinetic model was accomplished on the basis of the SPOIL function values¹⁶. The spectral data were analyzed with Excel 5.0, using Solver tool and macros developed especially for this purpose. Standard deviations of rate constants were evaluated using the procedure developed on the basis of the algorithm described by de Levie¹⁷.

RESULTS AND DISCUSSION

[PdCl(SnCl₃)L₂], where L = PPh₃ or P(*p*-Tol)₃, react with organic halides MeI, PhBr, PhCH₂Cl, or dichlorodimethylsilane to give tin-free complexes of palladium(II). The reactions of MeI, PhBr or PhCH₂Cl with [PdCl(SnCl₃)L₂] lead to the formation of [PdI(Me)L₂], [PdBr(Ph)L₂] and [PdCl(PhCH₂)L₂], respectively. Spectral data of these compounds agree with the literature data (¹H NMR, ³¹P NMR, IR)^{18–20}. The use of [PdCl(SnCl₃)L₂] as starting materials simplifies the preparation of organometallic complexes of palladium(II) (the air-unstable [Pd(PPh₃)₄] is eliminated) and the products are obtained in high yields (85–97%).

The reaction of [PdCl(SnCl₃)(PPh₃)₂] with Me₂SiCl₂ leads to obtained a new silyl complex of palladium(II) [PdCl(SiMe₂Cl)(PPh₃)₂]. The ¹H NMR of this compound consists of two signals, centered at 7.26 and 0.85 ppm. The multiplet at 7.26 is therefore assigned to the phosphine phenyl protons, while the singlet at 0.85 is assigned to silicon-bound methyl groups. The ³¹P NMR spectrum was not obtained, because the solubility of the product in CDCl₃ solution is too low for ³¹P NMR measurements. The IR spectrum of the compound contains numerous signals, most of which correspond to internal vibrations of the PPh₃ ligand. The IR spectrum displays two very intense and specific absorption bands at 1261 and 820 cm⁻¹ owing to the methyl groups bonded to silicon atom. Band characteristics of ν(Si–Cl) were also observed at 461 cm⁻¹. Within the region of 400–200 cm⁻¹, there are no bands characteristic of a coordinated trichlorostannate ligand²¹ and only a single strong peak at 348 cm⁻¹ corresponding to the ν(Pd–Cl) bond for the trans isomer was observed^{22,23}.

Kinetic studies of the reaction of [PdCl(SnCl₃)(PPh₃)₂] with Me₂SiCl₂ were carried out. The UV/VIS absorption spectrum of [PdCl(SnCl₃)(PPh₃)₂] in chloroform solution reveals a clearly resolved band at λ = 345 nm. A strong decrease in absorbance of this band, which can be treated as a measure of the unreacted substrate is a convenient way of checking progress of the reaction of chlorosilane with the metal complex. The change in character of the absorption spectrum occurring upon the reaction of [PdCl(SnCl₃)(PPh₃)₂] with Me₂SiCl₂ is illustrated in Fig. 1. Experimental runs were performed for Me₂SiCl₂ in chloroform solution varying from 0.05 to 10% in concentrations.

Factor analysis of the results showed that there were only two color components in the system (Fig. 2). The transformation of the abstract profiles taking into consideration only the condition of non-negativity of concentrations and absorbance for all the components leads to the profiles whose

shape suggests a course corresponding to the first-order kinetic equations $c = c_0 \exp(-k_{\text{obs}} t)$ for the substrate (Fig. 3) and $c = c_0[1 - \exp(-k_{\text{obs}} t)]$ for the product. The fit to the theoretical concentration profiles corresponding to this model allowed to obtain values of the SPOIL function less than six (Table I), i.e. a statistically acceptable model¹⁶.

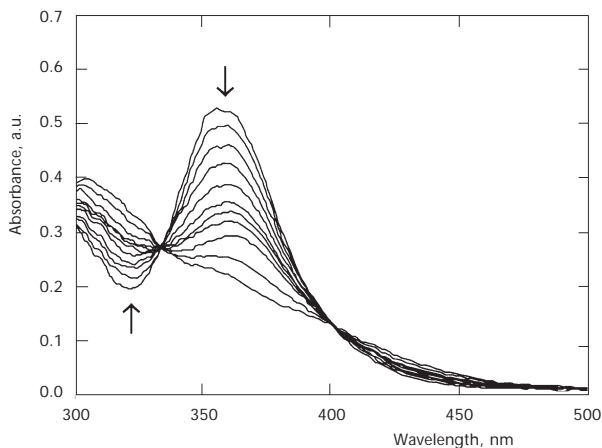


FIG. 1

Spectral changes during the reaction of $[\text{PdCl}(\text{SnCl}_3)(\text{PPh}_3)_2]$ ($c = 2 \times 10^{-3}$ mol/l) with Me_2SiCl_2 ($c = 0.135$ mol/l) for run 1. Reaction times (min): 0, 1.2, 3.4, 5.6, 7.8, 10.6, 12.8, 15, 20, 30 and 50

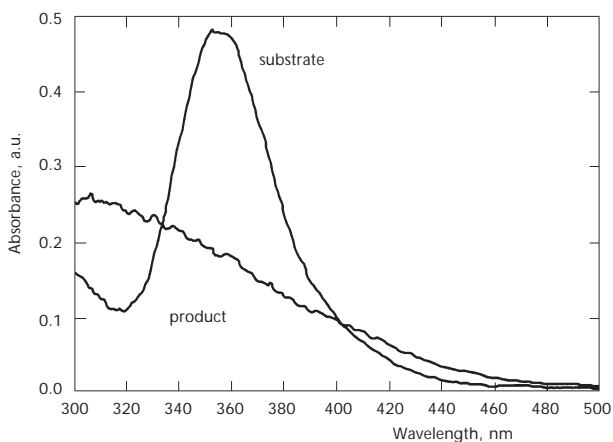


FIG. 2

Spectral profiles of the real components of the system $[\text{PdCl}(\text{SnCl}_3)(\text{PPh}_3)_2]$ ($c = 2 \times 10^{-3}$ mol/l)– Me_2SiCl_2 ($c = 0.267$ mol/l) for run 3

Spectrophotometric studies of the $[\text{PdCl}(\text{SnCl}_3)(\text{PPh}_3)_2]$ behavior in chloroform solution revealed that this complex undergoes a spontaneous intramolecular reduction, generating a metallic palladium. Kinetic study and factor analysis of this decomposition showed that this process runs in a way analogous to the reaction of $[\text{PdCl}(\text{SnCl}_3)(\text{PPh}_3)_2]$ with Me_2SiCl_2 (first-order reaction, $k_1 = (0.98 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$).

The values obtained for k_{obs} are similar to k_1 for spontaneous decomposition of the $[\text{PdCl}(\text{SnCl}_3)(\text{PPh}_3)_2]$ and roughly constant. Irregular and not large dependence of k_{obs} on chlorosilane concentration can be a consequence of incomplete deconvolution of spectral and concentration profiles for a consecutive reaction, if $k_2 > k_1$ ²⁴.

TABLE I
Results of chemometric analysis of the $[\text{PdCl}(\text{SnCl}_3)(\text{PPh}_3)_2]$ - Me_2SiCl_2 system; $[\text{Pd}] = 2 \times 10^{-3} \text{ mol/l}$

Run No.	Concentration of Me_2SiCl_2 mol/l	$k_{\text{obs}}, \text{ s}^{-1}$	SPOIL	
			for substrate	for product
1	0.135	$(1.3 \pm 0.2) \times 10^{-3}$	4.4	1.4
2	0.165	$(1.6 \pm 0.1) \times 10^{-3}$	3.3	5.8
3	0.267	$(1.1 \pm 0.1) \times 10^{-3}$	2.1	3.7
4	0.638	$(1.9 \pm 0.1) \times 10^{-3}$	1.9	2.5

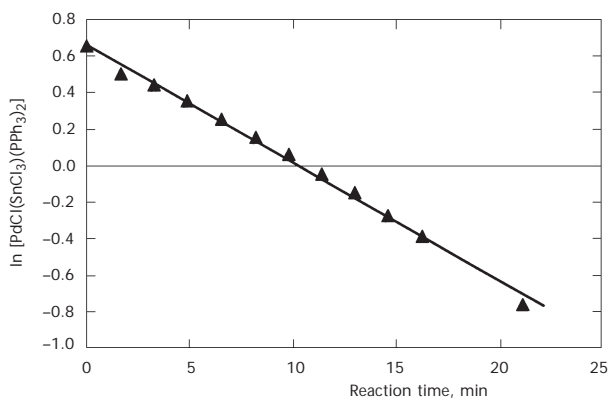
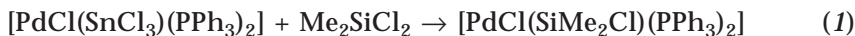


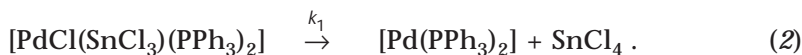
FIG. 3

The first-order plot of the decay of $[\text{PdCl}(\text{SnCl}_3)(\text{PPh}_3)_2]$ for run 3: $[\text{Pd}] = 2 \times 10^{-3} \text{ mol/l}$, $[\text{Me}_2\text{SiCl}_2] = 0.267 \text{ mol/l}$

From these observations and results (1) it has been concluded that the reaction



makes a consecutive process with the first monomolecular step being the rate determining. The first step of the interaction of $[\text{PdCl}(\text{SnCl}_3)(\text{PPh}_3)_2]$ with Me_2SiCl_2 is the intramolecular reaction (2) of Pd(II) with Sn(II) leading to the formation of coordinatively unsaturated complex $[\text{Pd}(\text{PPh}_3)_2]$



The next step is the fast oxidative addition (3) of Me_2SiCl_2 (with cleavage of the Si-Cl bond) and rapid formation of the final product



In conclusion, we have found a new rapid methodology to prepare the complexes of palladium(II), in high yields and under mild conditions. These new syntheses are reproducible and much more convenient than those previously reported. The proposed mechanism of the reaction suggests that the complexes of the $[\text{PdCl}(\text{SnCl}_3)_2]$ type can be attractive precursors of Pd(0) complexes in many catalytic processes.

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