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Reinvestigation of the Pd-catalyzed bis(silylation) of alkynes with 1,1,2,2-tetramethyl-1,2-bis(phenylthiomethyl)disilane: Unexpected formation of the eight-membered siloxane–chelate complex *cis*-$[PdCl_2\{(PhSCH_2SiMe_2)_2O\}]$

Harmel W. Peindy N'dongo [a,b], Sébastien Clément [b,*], Sébastien Richeter [b], Fabrice Guyon [a], Michael Knorr [a,*], Pierre le Gendre [c], Jonathan O. Bauer [d], Carsten Strohmann [d,**]

[a] *Institut UTINAM UMR CNRS 6213, Université de Franche-Comté, Faculté des Sciences et des Techniques, 16 Route de Gray, 25030 Besançon, France*
[b] *Institut Charles Gerhardt, UMR CNRS 5253, Equipe Chimie Moléculaire et Organisation du Solide, Place Eugène Bataillon, 34095 Montpellier Cedex 05, France*
[c] *Institut de Chimie Moléculaire, UMR CNRS 6302, Université de Bourgogne, 21078 Dijon, France*
[d] *Institut für Anorganische Chemie der Technischen Universität Dortmund, Otto-Hahn-Strasse 6, 44227 Dortmund, Germany*

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ABSTRACT

The bis(silylated) alkenes *Z*-$(PhSCH_2)Me_2SiC(H){=}C(Fc)SiMe_2(CH_2SPh)$ (**2**) and *Z*-$(PhSCH_2)Me_2SiC(H){=}C(bipheny)SiMe_2(CH_2SPh)$ (**3**) have been prepared by Pd-catalyzed double silylation of ethynylferrocene and 4-ethynyl-1,1′-biphenyl in the presence of 1,1,2,2-tetramethyl-1,2-bis(phenylthiomethyl)disilane (**1**). A reinvestigation on the interaction of **1** with $[PdCl_2(PhCN)_2]$ in technical-grade CH_2Cl_2 as solvent revealed competition between reduction to elemental palladium (due to oxidative addition of the Si–Si bond across Pd(II) and subsequent reductive elimination) and formation of an unusual eight-membered chelate complex *cis*-$[PdCl_2\{(PhSCH_2SiMe_2)_2O\}]$ (**4**), which is fluxional in solution. Based on GC–MS analyses revealing both formation of chlorosilane $ClSiMe_2CH_2SPh$ and the disiloxane $(PhSCH_2SiMe_2)_2O$, residual water contained in CH_2Cl_2 is supposed to be the source for the oxygen atom of the siloxane function. The mechanism of the formation of **4** is discussed. The molecular structures of **1** and **4** were determined by single-crystal X-ray diffraction analyses. The energies of several conformational isomers of **4** were computed by means of DFT calculations, the coexistence of a species featuring a weak dative Pd–O interaction due to a hemi-labile coordination of ligand **1** was evidenced.

1. Introduction

Disilanes, notably functionalized disilanes, are more and more used as versatile reagents in organometallic coordination chemistry and catalytic transformations. For example, $HR_2Si{-}SiR_2H$ (R = Me, Ph) have been used in oxidative addition reactions across $[(MeCp)Mn(CO)_2(THF)]$, $[CpRe(CO)_2(THF)]$ and $[Fe(CO)_4PPh_3]$ for the synthesis of hydrido disilanyl complexes [1]. Disilanyl complexes $[CpM(CO)_3Si_2Me_5]$ (M = Cr, Mo, W) have also been alternatively prepared by reaction of $[CpM(CO)_3]Na$ with Me_5Si_2Cl [2–4]. In the course of these stoichiometric reactions, a cleavage of the Si–Si bond of disilanes may also occur. For example, treatment of $HMe_2Si{-}SiMe_2H$ with $[Pt(PEt_3)_3]$ has led to the bis(silyl) complex *cis*-$[Pt(HMe_2Si)_2(PEt_3)_2]$ [5]. Even the unactivated disilane hexamethyldisilane can be oxidatively added across $[Pt(PEt_3)_3]$ to provide *cis*-$[Pt(Me_3Si)_2(PEt_3)_2]$ [6]. The Pd-catalyzed reaction of aroyl chlorides with hexamethyldisilane using $[PdCl_2(PhCN)_2]$ as catalyst represents a high-yield synthetic route leading to aroylsilanes [7].

However, the most wide-spread application is the transition metal mediated bis(silylation) (also called double silylation) of unsaturated organic substrates such as alkynes, olefins, isocyanides, aldehydes and ketones. This elegant synthetic strategy allows facile transformation of these substrates to organosilicon compounds [8–12]. Notably, palladium catalysts such as $[Pd(PPh_3)_4]$, $[PdCl_2(PR_3)_2]$ or *in situ* generated $[Pd(CNR)_2]$ (obtained by reduction of $Pd(OAc)_2$ with isonitriles CNR) are currently used for the catalytic bis(silylation) of these substrates [13–21]. Recent theoretical investigations performed on the activation of Si–Si bond have revealed that oxidative addition is a facile process with almost no energy barrier [22]. Furthermore, the frontier orbitals (HOMO and LUMO) of the Si–Si bond have been postulated to possess similar properties to the C=C bond [23]. From

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* Corresponding author. Tel.: +33 3 81 66 62 70.
** Corresponding author.
E-mail addresses: sebastien.clement02@univ-montp2.fr (S. Clément), michael.knorr@univ-fcomte.fr (M. Knorr), mail@carsten-strohmann.de (C. Strohmann).

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a mechanistic point of view, three key steps are involved in the catalytic cycle:

(i) oxidative addition of the Si—Si bond across a metal centre,
(ii) insertion of the unsaturated substrate into a M—Si bond,
(iii) and finally reductive elimination producing the bis(silylated) substrate, possessing in the majority of cases a *syn*-arrangement of the two silyl substituents stemming from the disilane precursor.

The stability of some reaction intermediates has allowed to isolate species such as Pd(IV) bis-silyl complexes, which have even been characterized by X-ray diffraction [24].

In the context of our on-going interest on organosilicon derivatives and transition metal silyl complexes [25], we have recently investigated the coordination chemistry of silanes functionalized by phenylthiomethyl groups [26]. We have also prepared 1,1,2,2-tetramethyl-1,2-bis(phenylthiomethyl)disilane (**1**) and coordinated **1** via its dithioether functions as chelate or bridging ligand to a range of transition metals such as Pt, Re and Ru [27]. Furthermore we have demonstrated that the catalytic cleavage of the Si—Si bond by Ito's $Pd(OAc)_2$/CNR catalyst allows addition across the triple bond of phenylacetylene, *p*-tolylacetylene and (±)-4-ethynyl[2.2]paracyclophane to afford the corresponding bis(silylated) olefins, whose *Z*-stereochemistry has been confirmed by an X-ray diffraction study on *Z*-$(PhSCH_2)Me_2SiC(H){=}C(Ph)SiMe_2(CH_2SPh)$ [27,28]. In this work, we have extended our investigation on the palladium-catalyzed double silylation of **1** across ethynylferrocene, since the presence of an electrochemically active ferrocenyl moiety appeared attractive for further studies. The characterization of the products of the bis(silylation) reaction of ethynylferrocene and 4-ethynyl-1,1′-biphenyl by multinuclear NMR techniques is described along with a re-examination of the coordination chemistry of **1** in the presence of a stoichiometric amount of $[PdCl_2(PhCN)_2]$, giving rise to an unusual eight-membered Pd(II) chelate complex of composition *cis*-$[PdCl_2\{(PhSCH_2SiMe_2)_2O\}]$.

2. Results and discussion

2.1. Crystal structure of 1,1,2,2-tetramethyl-1,2-bis(phenylthiomethyl)disilane (*1*)

In order to better understand the reactivity of this versatile ligand, we have determined the crystal structure of **1**, which crystallizes in form of huge colourless blocks having space group $P2_1/n$ within the monoclinic crystal system. The crystal structure is presented in Fig. 1, the crystal and refinement data are listed in Table 1. In the centrosymmetric molecule, the Si—Si bond distance is somewhat shorter than in *fac*-$[\{RuCl_2(CO)_3\}_2\{\mu\text{-}(PhSCH_2)_2Si_2Me_4\}]$ (2.3264(1) vs. 2.3533(12) Å), where disilane **1** bridges two $Ru(CO)_3Cl_2$ fragments. Other examples of structurally characterized disilanes containing a S—C—SiMe$_2$—SiMe$_2$—C—S motif are $(TTF)_2(Si_2Me_4)$ (TTF = tetrathiafulvalene; 2.327(3) Å) and macrocyclic 3,3,4,4,8,8,9,9-octamethyl-1,6-dithia-3,4,8,9-tetrasilacyclodecane (2.3450(4) Å) [29]. There are neither intermolecular nor intramolecular interactions between the sulphur atoms and the silicon centres. The shortest intermolecular S···Si contact found in the molecular cell is of 5.341 Å. For 1-fluoro-1,2-dimethyl-2,2-diphenyl-1-(8-phenylthio-1-naphthyl)disilane, an intramolecular S···Si distance of 2.9668(6) Å has been reported, which is considerably shorter than the sum of the van der Waals radii between an S and an Si atom (3.90 Å) [30]. In the case of **1**, the intramolecular S···Si contact amounts to 3.016 Å. However, the S—C7—Si angle of 109.7(11)° and C8—Si—C9 angle of 110.91(12)° rule out any incipient penta-coordination of Si as encountered in the former disilane.

2.2. Bis(silylation) of ethynylferrocene and 4-ethynyl-1,1′-biphenyl

The straightforward double silylation of a series of terminal aromatic alkynes with the formation of olefins possessing a *syn*-arrangement of the two $SiCH_2SPh$ groups around the C═C double bond encouraged us to react **1** also with ethynylferrocene. This choice was driven by the well-known redox activity of the ferrocenyl unit, a feature that appears interesting for potential applications of the resulting silylated olefin.

The bis(silylation) reaction was performed under the same conditions as reported in our previous work [27,28]. A toluene solution of **1** was reacted with ethynylferrocene in presence of a catalytic amount of 1,1,3,3-tetramethylbutylisocyanide and palladium acetate (Scheme 1). The orange starting mixture turned rapidly dark red-brown upon heating at 100 °C. After one day, work up was completed by column chromatography allowing the isolation of pure **2** in 67% yield as an orange waxy solid. ESI-mass spectrometry revealed the expected molecular mass peak at $m/z = 573.1$ corresponding to $[M + H^+]$. The ^1H NMR spectrum of **2** in $CDCl_3$ displays two singlets at $\delta = 0.41$ and 0.48 ppm attributed to the $SiCH_3$ groups, the singlet resonances due to the methylene $SiCH_2$ protons appear at $\delta = 2.34$ and 2.43 ppm. The ferrocenyl signals are present as a singlet at $\delta = 4.20$ ppm assigned to unsubstituted Cp ring proton and two other unresolved signals at $\delta = 4.24$ and 4.44 ppm attributed to the substituted Cp ring (see Fig. S1 in the Supporting information). As expected for two unequivalent SiR_3 groups, distinct resonances are observed in the $^{29}Si\{^1H\}$ NMR spectrum at $\delta = -10.1$ and -6.7 ppm (Fig. 2). The biphenyl-substituted derivate *Z*-$(PhSCH_2)Me_2SiC(H){=}C(biphenyl)SiMe_2(CH_2SPh)$ (**3**) was prepared in a similar manner and isolated in 64% yield as a yellow waxy solid. The similarity of the ^1H and $^{29}Si\{^1H\}$ NMR data (see Experimental section) with those of **2** and *Z*-$(PhSCH_2)Me_2SiC(H){=}C(Ph)SiMe_2(CH_2SPh)$ indicates again a *cis*-arrangement around the vinylic double bond.

2.3. Synthesis of palladium complex *4*

The versatile coordination chemistry of ligand **1** across several transition metal centres [Re(I), Ru(II), Pt(II)] has recently been described by us [27]. In the case of *cis*-$[PtCl_2(PhCN)_2]$, treatment with **1** in technical dichloromethane has led at room temperature straightforwardly to the seven-membered chelate complex *cis*-$[PtCl_2\{(PhSCH_2)_2Si_2Me_4\}]$. We have also reported that for *cis*-$[PdCl_2(PhCN)_2]$ under identical reaction conditions, we failed to isolate a homologous complex *cis*-$[PdCl_2\{(PhSCH_2)_2Si_2Me_4\}]$. Instead, precipitation of large amounts of elemental Pd was noticed after some minutes. In light of some isolated Pd(II) and Pd(IV) silyl complexes, this reaction was reinvestigated in more details. Thus, $[PdCl_2(PhCN)_2]$ was treated with ligand **1** in technical dichloromethane solution at room temperature (Scheme 2). The initial orange solution turned rapidly to a dark mixture with slow precipitation of colloidal palladium. After stirring overnight and subsequent evaporation of all volatiles, extraction of the dark solid with diethyl ether afforded an orange solid. Recrystallization from a cold CH_2Cl_2/*n*-hexane mixture afforded pure *cis*-$[PdCl_2\{(PhSCH_2SiMe_2)_2O\}]$ (**4**) as orange crystals suitable for X-ray crystallography, albeit in quite low yield (20%) [31].

The IR spectrum recorded in KBr exhibits along with a strong Si—Me vibration at 1258 cm^{-1} an additional intense band at 1029 cm^{-1} corresponding to the Si—O—Si group. This unexpected presence of a siloxane unit was corroborated by an ESI-MS analysis (positive mode), displaying the molecular peak $[M]^+$ of complex **4** at $m/z = 556$. The ^1H NMR spectrum of **4** recorded at room temperature exhibits quite broad resonances for the $SiCH_3$, SCH_2, and SPh protons indicative for a dynamic behaviour in solution,

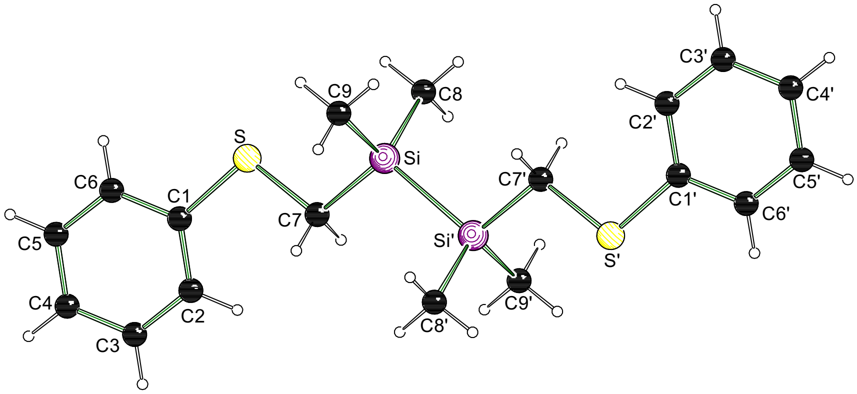
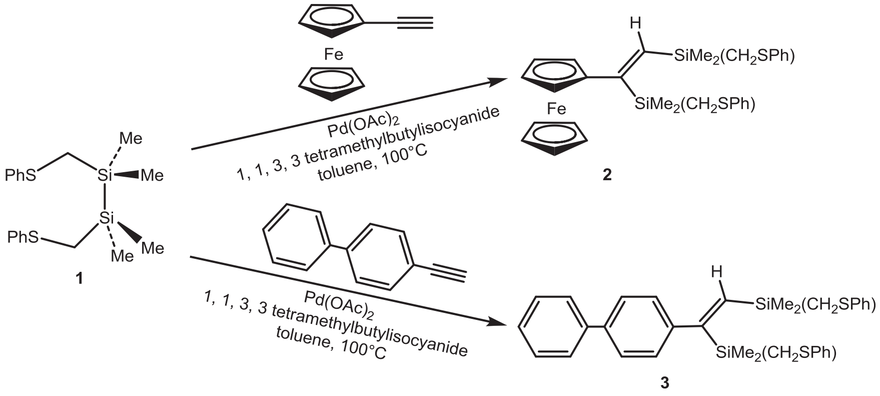


Fig. 1. SCHAKAL plot of disilane **1**. Selected bond lengths (Å) and angles (°). C(1)–C(2) 1.374(3), C(1)–S 1.768(2), C(7)–S 1.798(2), C(7)–Si 1.890(2), C(8)–Si 1.855(2), Si–Si′ 2.3264(11), C(2)–C(1)–C(6) 119.60(19), C(2)–C(1)–S 123.75(16), C(6)–C(1)–S 116.65(16), S–C(7)–Si 109.70(11), C(1)–S–C(7) 104.22(10), C(8)–Si–C(9) 110.91(12), C(9)–Si–Si′ 110.66(9). Symmetry transformations used to generate equivalent atoms: −x + 2, −y + 2, −z + 1.

which was monitored by variable-temperature ^{1}H NMR. At 213 K, resonances assigned to the Si–CH_3 groups appear as multiple singlets in the range between 0.32 and 0.65 ppm. The signals due to the methylene protons are more informative, since three AX systems of different intensities are observed between 1.88 and 3.59 ppm with $^2J_{H-H}$ couplings of 13 and 12 Hz, respectively. This observation reveals the presence of at least three isomers in solution in a 1/1.2/1.6 ratio. This is certainly in part due to the well-known pyramidal inversion of sulphur atoms occurring in square planar platinum and palladium dithioether complexes. The work of Abel et al. on this type of complexes has demonstrated that due to this phenomenon, two isomers (invertomers) exist in solution, which differ on the orientation of the S–R groups [32–34]. As shown in Scheme 2, the S–Ph groups are *cis*-arranged (*syn*) in the *u*-invertomer (*meso*-form), whereas they are *trans*-arranged (*anti*) in the *l*-invertomer. An activation energy ΔG$^\#$ of 70.2 kJ mol^{-1} has been determined for the inversion process occurring at the chelate complex *cis*-[PdCl$_2$(MeSCH$_2$CH$_2$SMe)] [32]. The temperature-dependent coexistence of several invertomers has been evidenced by us in the case of the related six- and seven-membered chelate complexes *cis*-[PtCl$_2${(PhSCH$_2$)$_2$SiPh$_2$}] and *cis*-[PtCl$_2${(PhSCH$_2$)$_2$Si$_2$Me$_4$}] by means of ^{195}Pt and ^{1}H NMR at variable temperature [26b,27]. But in case of complex **4**, the particular flexible Si–O–Si backbone confers additional conformational freedom. It is known, that even weakly coordinating siloxane oxygen atoms can bind in an intramolecular manner to Pd(II) [35]. Therefore, the presence of an additional isomer may be associated with a conformation involving a weak apical Pd···O contact. Indeed, this kind of incipient penta-coordination (*d* Pd···O = 2.968(3) Å) above the S$_2$PdCl$_2$ coordination plane of the complex *cis*-[PdCl$_2$ (1-oxa-4,7-dithiacyclononane)] has been evidenced by an X-ray study [36]. Although the shortest intramolecular Pd···O contact amounts

Table 1
Crystal and refinement data for compounds **1** and **4**.

Compound	**1**	**4**
Empirical formula	$C_{18}H_{26}S_2Si_2$	$C_{18}H_{26}Cl_2OPdS_2Si_2$
Formula weight [g mol^{-1}]	362.69	555.99
Temperature [K]	173(2)	173(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group (Nr.)	$P2_1/n$ (14)	$P2_1/n$ (14)
a [Å]	10.2511(7)	8.6216(17)
b [Å]	9.9931(5)	13.412(3)
c [Å]	10.4438(7)	19.858(4)
β [°]	111.570(8)	91.90(3)
Volume [Å^3]	994.94(11)	2295.0(8)
Z	2	4
Density (calculated) [g cm^{-3}]	1.211	1.609
Absorption coefficient [mm^{-1}]	0.383	1.334
F(000)	388	1128
Crystal size [mm^3]	0.20 × 0.10 × 0.10	0.30 × 0.20 × 0.10
Theta range for data collection [°]	2.38–27.00	2.55–25.99
Index ranges	$-13 \le h \le 13$ $-12 \le k \le 12$ $-12 \le l \le 13$	$-10 \le h \le 10$ $-16 \le k \le 16$ $-24 \le l \le 24$
Reflections collected	7953	21,171
Independent reflections	2174 (R_{int} = 0.0374)	4338 (R_{int} = 0.0350)
Refinement method	Full-matrix least-squares on F^2	
Data/Restraints/Parameters	2174/0/102	4338/0/239
Goodness-of-fit on F^2	1.000	1.008
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0360$, $wR2 = 0.0975$	$R1 = 0.0370$, $wR2 = 0.0974$
R indices (all data)	$R1 = 0.0536$, $wR2 = 0.1007$	$R1 = 0.0417$, $wR2 = 0.1056$
Largest diff. peak and hole [e Å^{-3}]	0.393 and −0.313	0.582 and −0.877



Scheme 1. Synthesis of the bis(silylated) olefins **2** and **3**.

to 3.626 Å in the solid-state structure of **4** (see below), other conformations allowing closer Pd···O contacts may be taken in consideration. Concerning the resonances due to the Ph groups, it is noteworthy that at low temperature a doublet at $\delta = 6.72$ ppm arises whereas there is no signal below 7.26 ppm at 293 K. This shielded resonance may result from a conformer with two perpendicular phenyl groups, such a conformation allowing the *ortho* H atoms of one phenyl to point towards the other aromatic cycle.

Taking the relatively high inversion barrier of three-coordinate sulphur atoms into account, two diastereomeric invertomers have to be considered in case of a stereochemically active lone pair (Fig. 3). Therefore, we performed DFT calculations on the B3LYP/6-31 + G(d) level regarding the two most plausible conformational isomers *l*-**4** and *u*-**4** (*meso*-invertomer), based on the molecular structure of **4** in the crystal that is exclusively found as the *l*-form (Fig. 4). The energetic gap between the two optimized invertomers accounts for only 13 kJ mol^{-1} with *l*-**4** being the energetically more stable invertomer. The calculations approve the coexistence of the two invertomers in solution in consequence of an interconversion equilibrium that presumably proceeds via an open form of **4**. Quantum chemical studies support the temporary appearance of an intermediate (**4**-Int) that is 85 kJ mol^{-1} higher in energy than *l*-**4** with a disconnected "hemi-labile" Pd–S bond and the siloxane oxygen atom now coordinating to the palladium centre, leading to a five-membered ring (Fig. 3, right). After rotation and reconnection of the sulphur atom to palladium, inversion and hence formation of the respective diastereomer is completed. Of course the classical inversion process without dissociation of a Pd–S bond may operate in parallel [32–34].

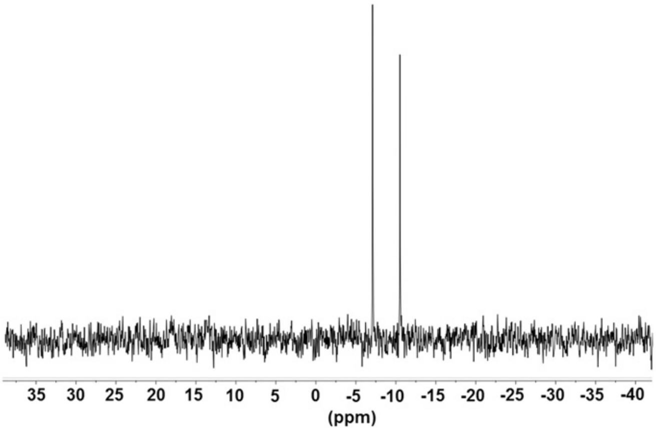
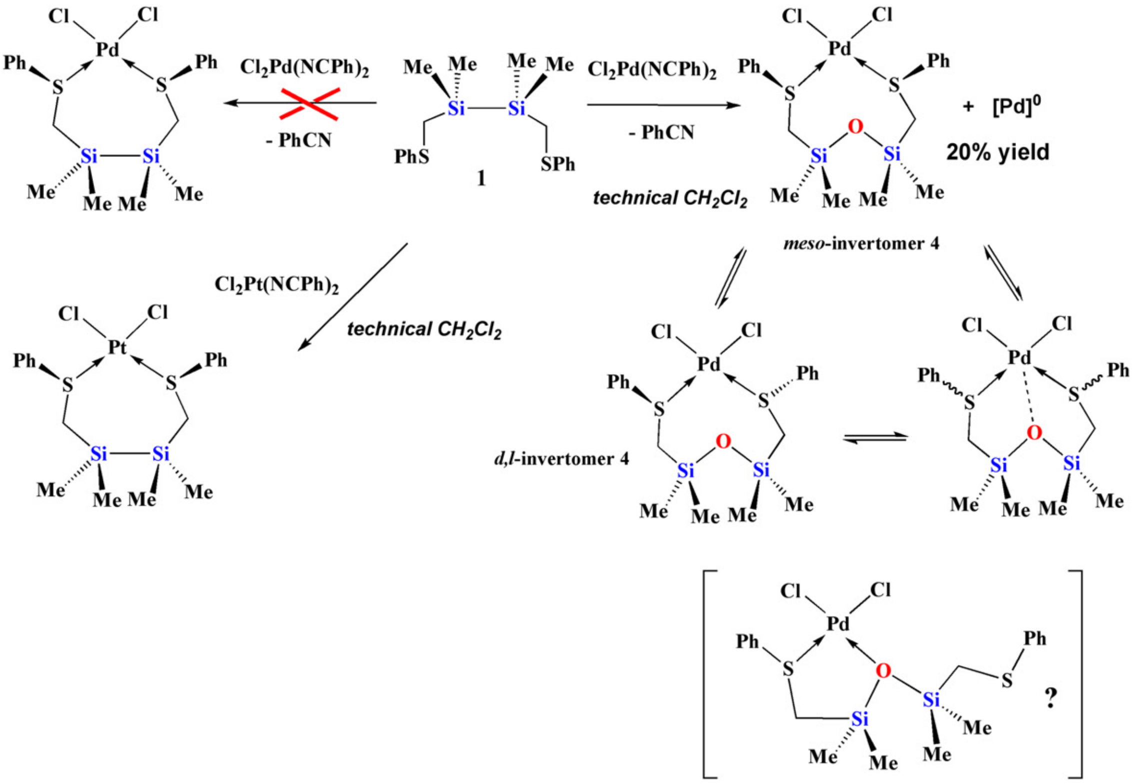


Fig. 2. $^{29}Si\{^{1}H\}$ NMR spectrum in $CDCl_3$ at 298 K of ferrocenyl compound **2**.

2.4. Crystal structure of complex 4

Fig. 4 shows the molecular structure of complex **4**, which crystallizes in the monoclinic crystal system, space group *P*2(1)/*n* (Table 1). The Pd(II) centre is coordinated by two sulphur atoms and two chlorine atoms in a square planar geometry. The two *cis*-arranged Cl atoms form an Cl(1)–Pd–Cl(2) angle of 90.96(3)°, the angle between the S atoms of 90.57(3)° also indicates no deformation. The RMS deviation from best plane comprising Cl(1), Cl(2) Pd, S(1) and S(2) amounts to 0.0343 Å. Within the dithioether ligand, the oxygen atom is inserted between the two silicon atoms of the disilane backbone of **1** forming a Si(1)–O–Si(2) angle of 144.18(15)°. The planes of the two phenyl groups adopt a nearly perpendicular orientation and are *anti*-arranged corresponding to the *l*-invertomer. The eight-membered ring adopts a boat-like conformation [C(1)–S(1)–Pd 110.53(10)°, C(2)–S(2)–Pd 107.50(11)°]. The Pd–S(1) and Pd–S(2) bond length of 2.3089(9) and 2.2974(8) Å are somewhat longer than the mean bond lengths of related chelate complexes *cis*-[$PdCl_2\{PhS(CH_2)_3SPh\}$] [2.284 Å] and *cis*-[$PdCl_2\{PhS(CH_2)_2SPh\}$] [2.263 Å] [37]. The average Pd–Cl bond length [2.31755 Å] lies in the usual range found for four-coordinate Pd(II) complexes [2.298–2.354 Å] [38]. The intramolecular Pd···O separation of 3.626 Å is far too remote even for a loose contact.

The surprising formation of a Pd(II) complex chelated by an eight-membered ring is quite unusual and deserves some comments. First of all, there are only very few precedents in the literature on transition metal complexes forming eight-membered chelates with acylic donor ligands. This bonding mode is less common compared to the plethora of five-, six-, and seven-membered systems due to the steric constraints imposed by an eight-membered cycle. Among the rare examples of eight-membered chelate complexes [39], there is the 1,5-bis(diphenylphosphino)pentane ligand, which coordinates to [$PdCl_2(NCPh)_2$] yielding *cis*-[$PdCl_2\{Ph_2P(CH_2)_5PPh_2\}$] [40]. Interestingly, the latter chelate complex undergoes upon heating a C–H activation reaction of the central methylene group forming the cyclometallated complex [$PdCl\{PPh_2CH_2CH_2CHCH_2CH_2PPh\}$] [40]. This creation of a Pd–C bond confirms our hypothesis, that in the case of **4** the siloxane O-atom can come close enough to Pd(II) to form species (**4**-Int) featuring a weak dative Pd–O bond as shown in Fig. 3. In the case of dithioether ligands, there is a report on the photochemically-induced complexation of 1,5-bis(*tert*-butylthio) pentane on $W(CO)_6$ to afford *cis*-[$W(CO)_4\{^{t}BuS(CH_2)_5S^{t}Bu\}$] [41].



Scheme 2. Synthesis of complex **4**.

However, addition of the ligand 1,5-bis(*tert*-butylthio)pentane to [$PdCl_2(NCPh)_2$] produces the mesocyclic 16-membered dinuclear complex *trans*-[$Pd_2Cl_4\{{}^tBuS(CH_2)_5S^tBu\}_2$] [42]. The ligand 1,5-bis(phenylthio)pentane, which is quite comparable to ligand **1**, coordinates to [$PdCl_2(NCPh)_2$] forming the 1D coordination polymer *trans*-[$PdCl_2\{PhS(CH_2)_5SPh\}]_n$ [43]. This contrasting behaviour in the coordination of the latter dithioether and ligand **1** upon complexation on Pd(II) could probably be rationalized by the higher conformational flexibility of the C–Si–O–Si–C spacer compared to a C–C–C–C–C spacer, such diminishing steric constraints in the cycle. Furthermore, coordination of the central siloxane O-atom giving first rise to an intermediate five-membered chelate complex (see Scheme 2), which subsequently rearranges into an eight-membered ring, may also explain the diverging coordination modes between the 1,5-bis(phenylthio)pentane and ($PhSCH_2$)Me_2Si–O–$SiMe_2$(CH_2SPh) ligands.

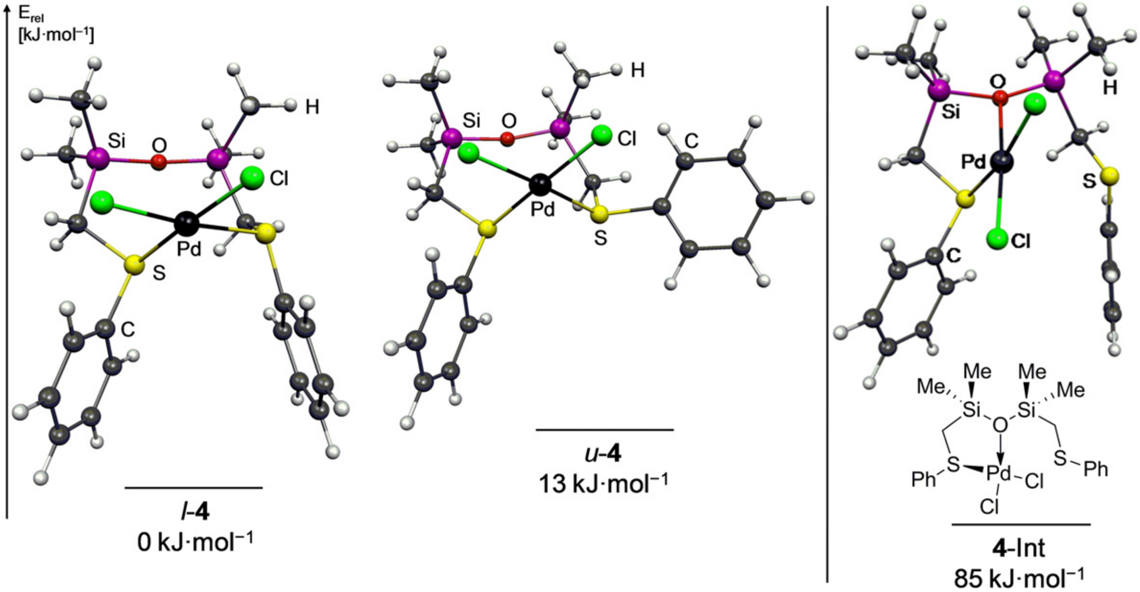


Fig. 3. Optimized structures of the two diastereomeric invertomers *l*-**4** and *u*-**4** (left) and the five-membered interconversion intermediate **4**-Int (right) [B3LYP/6-31 + G(d)].

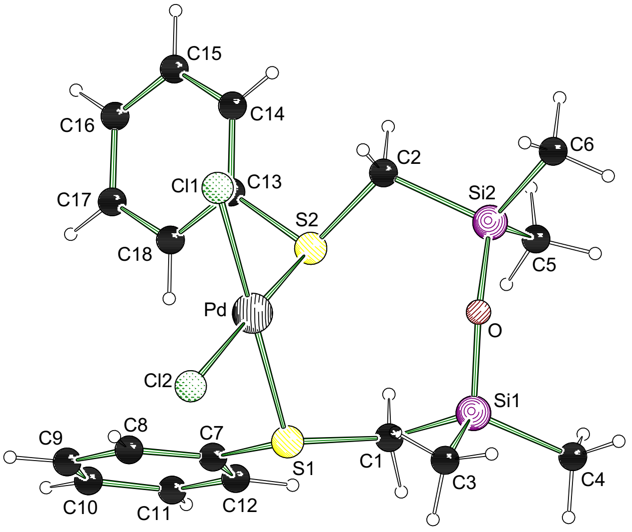


Fig. 4. SCHAKAL plot of complex **4**. Selected bond lengths (Å) and angles (°). Pd–S(2) 2.2974(8), Pd–S(1) 2.3089(9), Cl(1)–Pd 2.3116(9), Cl(2)–Pd 2.3235(9), O–Si(1) 1.640(2), O–Si(2) 1.644(2), C(1)–Si(1) 1.895(3), C(2)–S(2) 1.790(3), C(2)–Si(2) 1.903(3), C(3)–Si(1) 1.850(3), C(7)–S(1) 1.791(3), Si(1)–O–Si(2) 144.18(15), S(2)–Pd–S(1) 90.57(3), S(2)–Pd–Cl(1) 92.28(3), S(1)–Pd–Cl(1) 176.79(3), S(2)–Pd–Cl(2) 176.07(3), S(1)–Pd–Cl(2) 86.25(3), Cl(1)–Pd–Cl(2) 90.96(3), C(7)–S(1)–C(1) 106.57(14), C(7)–S(1)–Pd 103.50(10), C(1)–S(1)–Pd 110.53(10), C(2)–S(2)–Pd 107.50(11), C(13)–S(2)–Pd 108.94(10), O–Si(1)–C(4) 112.11(15), O–Si(2)–C(5) 110.37(14).

*2.5. Discussion on the formation mechanism of complex **4***

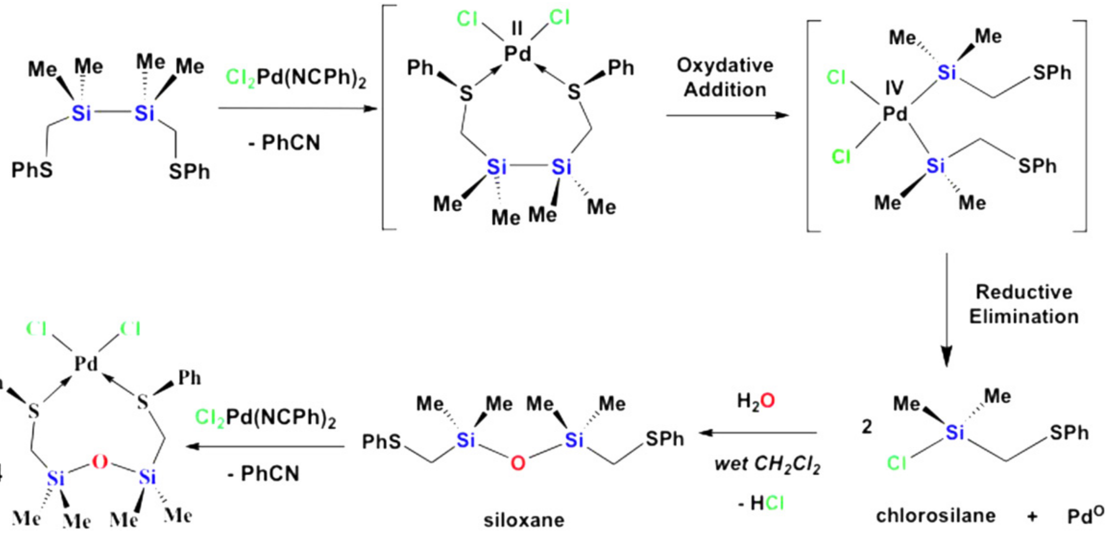
We suggest the following mechanism to rationalize the unexpected formation of complex **4** bearing a chelating $(PhSCH_2SiMe_2)_2O$ ligand (Scheme 3). After initial coordination of the dithioether on Pd(II) forming a seven-membered chelate analogous to *cis*-$[PtCl_2\{(PhSCH_2)_2Si_2Me_4\}]$, oxidative addition of the Si–Si bond occurs to yield an labile Pd(IV) intermediate. This latter may then get reduced via reductive elimination of chlorosilane $ClSiMe_2(CH_2SPh)$, thus explaining the formation of elemental palladium. Chlorodimethyl(phenylthiomethyl)silane in turn gets hydrolyzed by small amounts of H_2O present in technical grade dichloromethane to give rise to a disiloxane by condensation of the silanol groups. Both the presence of the chlorosilane and disiloxane has been confirmed by GC/MS experiments (see below). Finally, the disiloxane-derived dithioether $(PhSCH_2)Me_2Si–O–SiMe_2(CH_2SPh)$ coordinates on unreacted $[PdCl_2(PhCN)_2]$ through its sulphur atoms to account for the formation of eight-membered chelate complex *cis*-$[PdCl_2\{(PhSCH_2SiMe_2)_2O\}]$ (**4**).

Our mechanistic suggestion is supported by the following facts and observations:

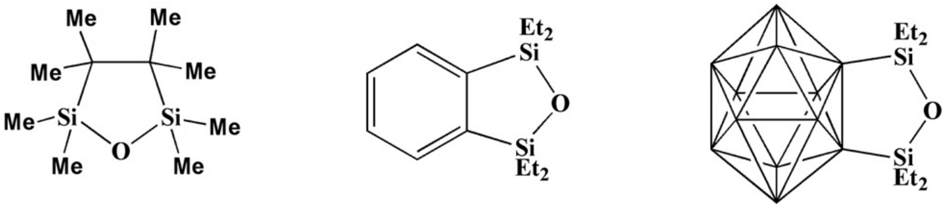
(i) As already mentioned above, silyl complexes of Pd(IV) have been characterized by X-ray crystallography studies [24,44]. The formation of an intermediate Pd(IV) bis(silyl) complex has also been postulated by Seyferth et al. to explain the formation of $ClSiMe_2CMe_2CMe_2SiMe_2Cl$ upon treatment of octamethyl-l,2-disilacyclobutane with a stoichiometric amount of $[PdCl_2(PPh_3)_2]$ [16d].

(ii) To exclude the possibility that the SPh groups are involved during the oxidative addition/reductive elimination steps, the reaction of non-activated hexamethyldisilane with an equimolar amount of $[PdCl_2(PPh_3)_2]$ in technical-grade CH_2Cl_2 was examined. Again, a rapid precipitation of colloidal Pd was noticed. IR analysis revealed that formation of $Me_3SiOSiMe_3$ occurred. The formation of $ClSiMe_3$ was evidenced in an indirect manner by the liberation of HCl liberated during the hydrolysis of $ClSiMe_3$. Independently from our experiment, the same result has been recently reported by Kashiwabara and Tanaka, who conducted this reaction in toluene and detected formation of $ClSiMe_3$ by ^{29}Si NMR within 5 min after mixing the starting materials [45].

The reaction of disilane ligand **1** with $[PdCl_2(PhCN)_2]$ in dry dichloromethane at room temperature was also repeated and its evolution monitored by GC–MS analysis through diluted sample measurements. Typically, an analytical sample was collected from the reaction mixture (100 μL) and diluted with additional CH_2Cl_2 solution (100 μL) prior to the injection. After a running time of 15 min, GC–MS analysis revealed a peak at $m/z = 103$ assigned to the decomplexation of benzonitrile from the Pd(II) centre and a second peak at $m/z = 216$, attributed to $PhSCH_2SiMe_2Cl$ resulting from reductive elimination of a Pd(IV) intermediate. Analysis of the reaction mixture after 2 h showed a main peak at $m/z = 216$ due to the chlorosilane, the remaining benzonitrile ligand at $m/z = 103$



Scheme 3. Supposed formation mechanism of compound **4**.



Scheme 4. Examples of some cyclic siloxanes.

and the disilane **1** at $m/z = 362$. No significant evolution of the chromatogram was noticed after 24 h and 48 h. However, when 100 μL of a sample in dry dichloromethane solution was collected and diluted with 100 μL of technical-grade dichloromethane, GC–MS analysis indicated a new peak at $m/z = 379$ assigned to the siloxane $(PhSCH_2SiMe_2)_2O$ formed by intermolecular condensation of two chlorosilane molecules in presence of water to give the disiloxane (see Fig. S4 in the Supporting information).

(iii) It is literature-known that oxygen insertion into a Si–Si bond leading to a siloxane may also occur by exposure to air, peroxide, tertiary amine oxide or water [46–48]. For instance, Seyferth et al. have reported the exothermic hydrolysis of octamethyl-1,2-disilacyclobutane by adding deoxygenated water to form almost quantitatively 2,2,3,3,4,4,5,5-octamethyl-1-oxa-2,5-disilacyclopentane [16d]. Thermal treatment of 3,4-carboranylene-1,1,2,2-teraethyl-1,2-disilacyclo-but-3-ene in air-containing toluene solution resulted also in the formation of the cyclic siloxane 4,5-carboranylene-1,3-disila-2-oxacyclopent-4-ene (Scheme 4) [49].

However, no conversion of $[PtCl_2\{(PhSCH_2)_2Si_2Me_4\}]$ in CH_2Cl_2 solution upon prolonged exposure to air was noticed. Furthermore, when ligand **1** was treated with *cis*-$[PdCl_2(PhCN)_2]$ in dry CH_2Cl_2 under O_2 atmosphere, there was no evidence of the formation of complex **4**. Therefore, direct oxygen insertion into an initially formed chelate complex $[PdCl_2\{(PhSCH_2)_2Si_2Me_4\}]$ can be excluded to explain formation of **4**.

(iv) The last step of the proposed reaction sequence shown in Scheme 3, namely coordination of $(PhSCH_2SiMe_2)_2O$ on $[PdCl_2(PhCN)_2]$, was proven by independent synthesis of this siloxane. This latter was prepared by treatment of dimethyldichlorosilane with one equivalent of $LiCH_2SPh$ [50a], and subsequent hydrolysis of the resulting chlorosilane $PhSCH_2SiMe_2Cl$ [50b]. Indeed, coordination of this siloxane on $[PdCl_2(PhCN)_2]$ in CH_2Cl_2 solution afforded readily chelate complex **4** in an improved yield of 61%.

3. Conclusion

We have shown that Pd-catalyzed double silylation of disilane ligand **1** can also be applied to functionalized terminal alkynes such as ethynylferrocene to provide the alkenyl-dithioether *Z*-$(PhSCH_2)Me_2SiC(H)$=$C(Fc)SiMe_2(CH_2SPh)$ (**2**). Since ferrocenyl-dithioethers represent interesting redox-active metalloligands [51], we are currently exploiting the propensity of **2** to assemble polymetallic system and coordination polymers. To enlarge the range of available alkenyl-dithioether ligand, we are currently probing the addition of **1** across terminal aliphatic alkynes. We have furthermore shown in this study that oxidative addition of disilane **1** occurs also across $[PdCl_2(PhCN)_2]$ even at ambient temperature producing the unusual fluxional 8-membered dithioether complex *cis*-$[PdCl_2\{(PhSCH_2SiMe_2)_2O\}]$ (**4**). The unexpected formal insertion of an oxygen atom into the Si–Si bond of **1** has been mechanistically elucidated. Complex **4** has been alternatively prepared in an improved yield by treatment of $[PdCl_2(PhCN)_2]$ with the siloxane $(PhSCH_2SiMe_2)_2O$.

4. Experimental section

4.1. General procedures

Reactions were performed in oven-dried Schlenk glassware under an atmosphere of pure nitrogen when necessary. Solvents were dried over molecular sieves and degassed prior to use. IR spectra have been recorded on a Nicolet Nexus 470 spectrometer. NMR spectra were recorded on Bruker Advance 300 spectrometers. Chemical shifts δ are given in ppm relative to tetramethylsilane and coupling constants J are given in Hz. The GC/MS system consists of a Shimadzu GC-2010 gas chromatograph with Solution software 2.10. The column was a 25 m long FS-OV1-CB-0.25 column with 0.25 mm ID and 0.36 mm film thickness with a temperature maximum between 300 and 320 °C. The carrier gas was 99.995% pure helium used at a flow rate of 1.06 mL min^{-1} (40.8 cm s^{-1}) with a head pressure of 9.4 psi at 40 °C. The sample in CH_2Cl_2 solution was injected manually using a splitless mode and the injection volume was 1 μL. Temperatures of the injection port and mass selective detector interface were set at 150 and 200 °C, respectively. The temperature gradient of the GC oven was programmed to be initiated at 60 °C for 2 min, then raised to 290 °C at 10 °C min^{-1} and held at the final temperature for 5 min. An electron impact (EI) ionization mode with 1.5 kV absolute voltage detector was used.

*4.2. General procedure for the synthesis of bis(silylated) compounds **2** and **3***

To a toluene solution (10 mL) containing **1** (181 mg, 0.50 mmol), ethynylferrocene or 4-ethynylbiphenyl (0.70 mmol) and palladium acetate (2 mg, 0.01 mmol) was added 1,1,3,3-tetramethylbutylisocyanide (27.8 mg, 0.2 mmol). The yellow mixture quickly turned dark red after heating to 100 °C. Stirring was continued for 1 d, and then all volatiles were removed under reduced pressure. The residue was purified by column chromatography with CH_2Cl_2/*n*-hexane (1:9) as eluent affording **2** or **3** in 67 and 64% yield, respectively.

2: Anal. Calcd for $C_{30}H_{36}FeS_2Si_2$ (572.1) C, 62.91; H, 6.34, S, 11.20. Found: C, 62.78; H, 6.26, S, 11.01. ^1H NMR: δ 0.41 (s, 6H, $SiCH_3$), 0.48 (s, 6H, $SiCH_3$), 2.34 (s, 2H, $SiCH_2SPh$), 2.43 (s, 2H, $SiCH_2SPh$), 4.20 (s, 5H, Cp), 4.24 (s, br, 2H, Cp), 4.44 (s, br, 2H, Cp), 7.13–7.19 (m, 2H, Ph), 7.29–7.42 (m, 9 H, Ph + =CH) ppm. $^{13}C\{^1H\}$ NMR: δ 0.0, 0.2 ($SiCH_3$), 18.9, 19.8 (1C, $SiCH_2S$), 68.0, 69.2, 70.1 (Cp), 125.0, 125.2, 126.6, 126.7, 129.1, 129.2, 140.5, 140.6, 145.8, 159.2 ppm. $^{29}Si\{^1H\}$ NMR: δ −10.1 (s, 1 Si), −6.7 (s, 1 Si) ppm. ESI-MS (m/z): 573.1 (M + H).

3: Anal. Calcd for $C_{32}H_{36}S_2Si_2$ (542.2) C, 71.05; H, 6.71, S, 11.86. Found: C, 70.82; H, 6.51, S, 11.79. ^1H NMR: δ 0.42 (s, 6H, $SiCH_3$), 0.48 (s, 6H, $SiCH_3$), 2.34 (s, 2H, $SiCH_2SPh$), 2.41 (s, 2H, $SiCH_2SPh$), 6.69 (s, 1H, =CH), 7.10–7.68 (m, 19H, Ph) ppm. $^{13}C\{^1H\}$ NMR: δ −0.25, −0.19

($SiCH_3$), 19.0, 19.2 (1C, $SiCH_2S$), 125.2, 125.3, 126.3, 126.6, 126.7, 126.8, 127.0, 128.1, 129.0, 129.1, 129.2, 139.4, 141.2, 143.9, 148.0, 149.0, 163.7 ppm. $^{29}Si\{^1H\}$ NMR: δ −9.84 (s, 1 Si), −6.83 (s, 1 Si) ppm. ESI-MS (*m*/*z*): 541.1 (M + H).

4.3. Preparation of cis-$[PdCl_2\{(PhSCH_2SiMe_2)_2O\}]$(**4**)

Method A. To a solution of $[PdCl_2(PhCN)_2]$ (192 mg, 0.50 mmol) in 10 mL of technical-grade dichloromethane was added **1** (182 mg, 0.50 mmol). The yellow solution turned rapidly brown and precipitation of Pd was noticed. After stirring overnight, all volatiles including liberated benzonitrile were removed under *vacuo*. The dark solid was then extracted with several portions of diethyl ether (3 × 5 mL) and separated from the resulting suspension by filtration. From the combined fractions, an orange solid was isolated. This latter was then re-dissolved in 3 mL of CH_2Cl_2 and a *n*-hexane layer was added. Orange crystals (57 mg, 20% yield) suitable for X-ray diffraction were obtained. *Method B*. To a solution of $[PdCl_2(PhCN)_2]$ (192 mg, 0.50 mmol) in 5 mL of dichloromethane was added $(PhSCH_2SiMe_2)_2O$ (228 mg, 0.60 mmol). The yellow solution turned rapidly to red-orange. After stirring for 2 h, 6 mL of *n*-heptane were added and the solution concentrated under reduced pressure to ca. 5 mL. After keeping at 5 °C, a first crop of spectroscopically pure microcrystalline **4** was obtained. A second crop was isolated after storing the filtered solution at −20 °C. Overall yield: 170 mg (61%).

Anal. Calcd for $C_{18}H_{26}Cl_2OPdS_2Si_2$ (555.99): C, 38.88; H 4,71. Found: C, 38.64; H 4.68%. ^1H NMR ($CDCl_3$, 213 K): δ 0.32–0.65 (m, $SiCH_3$), 1.85 (d, 11.9 Hz, CH_2), 1.89 (d, 13.1 Hz, CH_2), 2.02 (d, 12.6 Hz, CH_2), 2.94 (d, 12.6 Hz, CH_2), 3.34 (d, 11.9 Hz, CH_2) 3.60 (d, 13.1 Hz, CH_2), 6.62–7.87 (m, Ph) ppm. IR (KBr, cm^{-1}) 1258, 1029.

4.4. X-ray crystallography

Suitable crystals of **1** and **4** were covered with an inert oil (perfluoropolyalkylether) and used for X-ray crystal structure determination. X-ray diffraction data of the structures **1** and **4** were recorded at 173(2) K with the Oxford Diffraction Xcalibur S diffractometer (**1**) and the Stoe IPDS diffractometer (**4**). Graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) was used. The crystal structures were solved with direct methods (*SHELXS97*; Sheldrick, 2008) and refined against F^2 with the full-matrix least-squares method (*SHELXL97*; Sheldrick, 2008). A multi-scan absorption correction using the *CrysAlis RED* program (Oxford Diffraction, 2006) (**1**) and a numerical absorption correction using the *FACEIT* program in IPDS (Stoe & Cie, 1999) (**4**) was employed. The non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were placed in geometrically calculated positions and each was assigned a fixed isotropic displacement parameter based on a riding-model. Information concerning the data collection and processing, crystallographic parameters and details on structure solution and refinement are given in Table 1. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 886242 (**1**) and CCDC 886243 (**4**). Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; [fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

4.5. Computational details

Optimization and additional harmonic vibrational frequency analyses were performed with the software package Gaussian 03 (Revision E.01) on the B3LYP/6-31 + G(d) [52] level using pseudopotentials ECP28MWB for palladium. The total (SCF) and zero-point energies (ZPE) of the calculated systems can be found in Table SI 1. The calculated standard orientations of the optimized molecules *l*-**4**, *u*-**4** and **4**-Int are summarized in Tables SI 2–SI 4 in the Supporting information.

Acknowledgements

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Appendix A. Supporting information

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2012.11.022.

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work up was hampered by the difficult separation of unreacted [$PdCl_2(PhCN)_2$] and **4**.

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(b) $(PhSCH_2SiMe_2)_2O$ was obtained by the following manner: Addition of (phenylthiomethyl)lithium, prepared from thioanisole (1.0 eq., 5.0 g, 40.3 mmol) and *n*-BuLi (1.1 eq., 17.7 mL of a 2.5 M solution in cyclohexane, 44.3 mmol) in 15 mL diethyl ether, at 0 °C, to a solution of dichlorodimethylsilane (1.1 eq., 5.70 g, 44.3 mmol) in 5 mL of diethyl ether at −40 °C afforded first $PhSCH_2SiMe_2Cl$. Subsequent hydrolysis of this chlorosilane yielded the targeted siloxane in 85% purity as colourless oil. ^1H, $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectroscopic analysis of the crude product revealed the presence of small amounts of $(PhSCH_2)_2SiMe_2$ and $(SiMe_2)O_n$ as by-products. ^1H NMR (400.1 MHz, $CDCl_3$): δ 0.35 (s, 12H, $SiCH_3$), 2.32 (s, 4H, $SiCH_2SPh$), 7.14–17.38 (m, 10H, Ph) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 0.35 (4C, $SiCH_3$), 19.33 (2C, $SiCH_2S$), 124.63, 126.09, 128.62, 139.84 (4C, Ph) ppm. $^{29}Si\{^1H\}$ NMR (59.6 MHz, $CDCl_3$): δ 5.38 (s, 2Si) ppm.

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