Reactivity of the bis(silyl) palladium(II) complex toward organic isothiocyanates

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ABSTRACT

The bis(silyl) palladium(II) complex $[Pd(SiHPh_2)_2(dmpe)]$ (dmpe = 1,2-bis(dimethylphosphino)ethane) reacted with organic isothiocyanates R–NCS (R = Ph, ^iPr, allyl) to give a dithiocarbonimidato $[Pd(S_2C=N-Ph)(dmpe)]$ (1), a diphenylsilanedithiolato $[Pd(S_2SiPh_2)(dmpe)]$ (2), or a π-allyl $[(\eta^3\text{-allyl})Pd](NCS)$ (3) palladium complex, depending on the isothiocyanate type and reaction conditions. In addition, various dithiocarbonimidato Pd(II) complexes were also obtained from trans-$[PdEt_2L_2]$ (L = PMe$_3$, PMe$_2$Ph) (4–6) or $[Pd(styrene)L_2]$ and organic isothiocyanates.

1. Introduction

A stoichiometric or catalytic insertion of an organic unsaturated compound into the M−Si bond in bis(silyl)−(group 10 metal) complexes is a key step to generate a silyllated organic compound [1–25]. Whereas insertion reactions of alkenes, alkynes, and dienes are well established, those of isonitriles (R−NC), nitriles (R−CN), and isothiocyanates (R−NCS) are still rare [26–29]. Recently, we reported that bis(silyl) Pt(II) complexes $[Pt(SiHPh_2)_2L_2]$ (L = tertiary phosphine) reacted with isothiocyanates to afford the dithio-carbonimidato−Pt(II) complexes {$[Pt(S_2C=NR)L_2]$ or diphenylsila-nedithiolato−Pt(II) complexes $[Pt(S_2SiPh_2)L_2]$}, depending on the reaction temperature, the stoichiometry, and the nature of the phosphine ligand. [29]. As an extension of this study, we investi-gated the corresponding reactivity of the Pd analogue, $[Pd(SiHPh_2)_2(dmpe)]$.

We report herein the selective formation of the novel dithiocarbonimidato− and diphenylsilanedithiolato−Pd(II) complexes, $[Pd(S_2C=NR)L_2]$ and $[Pd(S_2SiPh_2)L_2]$, from $[Pd(SiHPh_2)_2(dmpe)]$ and R−NCS. In order to confirm whether the dithiocarbonimidato compound $[Pd(S_2C=NR)L_2]$ can be formed by an alternative route, we also examined the reactivity of iso-thiocyanates with $[PdEt_2L_2]$, which may serve as a source of a Pd(0) species.

2. Results and discussion

$[Pd(SiHPh_2)_2(dmpe)]$ reacted with 2 equiv of Ph−NCS at 50 °C for 6 h in THF to give the dithiocarbonimidato Pd(II) complex $[Pd(S_2C=N-Ph)(dmpe)]$ (1) in 77% yield (Eq. (1)). The same reaction of 1 or 2 equiv of Ph−NCS at room temperature did not go to completion and gave a mixture of complex 1 and an unique diphenylsilanedithiolato complex $[Pd(S_2SiPh_2)(dmpe)]$, 2 and a starting material. On the other hand, when the reaction was carried out with isopropyl isothiocyanate (^iPr−NCS) in place of Ph−NCS at room temperature, only complex 2 was obtained in 59% yield (Eq. (2)). Complexes 1 and 2 were characterized by IR and NMR (^1H, ^{13}C, and ^{31}P) spectroscopy, and elemental analyses. The IR spectra of complex 1 clearly display a new ν(N=C) band at 1553 cm^{-1} assignable to the $S_2C=N-R$ group, without the ν(Si−H) band at 2038 cm^{-1} present in the starting material. ^{31}P NMR spectra of complexes 1 and 2 show two doublets and one singlet, respectively, due to magnetic nonequivalence or equivalence of the two PR$_2$ groups. The structure of complex 2 was unambiguously determined by X-ray diffraction.
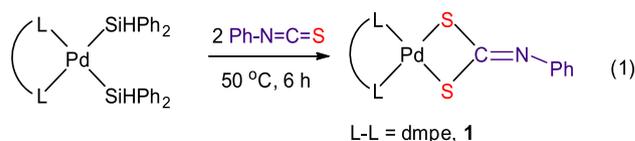
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(1)

$$\text{(2)}$$

$$\text{L-L = dmpe, R = }^{i}\text{Pr, 2}$$
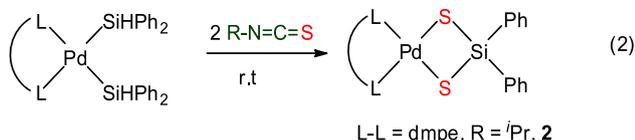
Interestingly, when [Pd(SiHPh$_2$)$_2$(dmpe)] is treated with 2 equiv of allyl isothiocyanate at room temperature, [(η^3-allyl)Pd(dmpe)] (NCS) (**3**) is formed in 58% yield as white crystals (Eq. (3)). The chemical formula of complex **3** indicates that the two SiHPh$_2$ ligands were eliminated and the C—N bond in the allyl isothiocyanate was cleaved to generate the η^3-allyl ligand and the NCS counter ion. On the other hand, the dithiocarbonimidato complex M(S$_2$C=N—allyl), an analogue of complex **1**, is not observed. The ^{1}H NMR spectrum of complex **3** displays the peaks at δ 3.78 and 5.38 due to CH$_2$ and CH signals, respectively, characteristic of the π-allyl ligand. A singlet in the ^{31}P NMR strongly supports the magnetic equivalence of the PR$_2$ groups in the dmpe ligand due to the high-symmetric structure of complex **3**, which was also confirmed by X-ray diffraction.

$$\text{(3)}$$
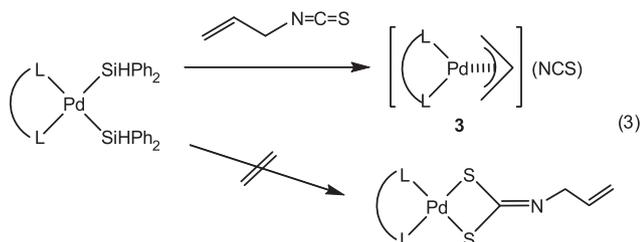
We previously observed that [Pt(SiHPh$_2$)$_2$(PR$_3$)$_2$], a Pt analogue of the present study, reacted with Ar—NCS to afford the dithiocarbonimidato Pt(II) complexes [Pt(S$_2$C=N—Ar)L$_2$] or the diphenylsilanedithiolato Pt(II) complexes Pt(S$_2$SiPh$_2$)$_2$(PR$_3$)$_2$, depending on the organic substrates used and supporting ligands [29]. Our current results are basically the same as those observed for the Pt (II) complexes; that is, the formation of dithiocarbonimidato— or diphenylsilanedithiolato—Pd(II) complexes depends on the substituents in the reacting isothiocyanates (aromatic versus aliphatic). On the other hand, several Pd(0) complexes such as [Pd$_2$(dba)$_3$]·CHCl$_3$ [30] (in the presence of PPh$_3$) and [Pd(PR$_3$)$_n$] [31] (n = 4 for PMe$_3$, PMe$_2$Ph, PMePh$_2$; n = 2 for P(i-Pr)$_3$) were shown to react with R—NCS (R = Me, Ph, C(O)OEt) to give only the dithiocarbonimidato Pd complexes [Pd(S$_2$C=N—R)(PR$_3$)$_2$]. Several earlier works also showed that the low-oxidation-state Pt [32], Ru [33] and Rh [34] species reacted with isothiocyanates (R—NCS; R = Me, Ph, C (O)OEt), in the presence of excess R—NCS, to produce the dithiocarbonimidato complexes [M(S$_2$C=N—R)] by the π-coordination of R—NCS and the (subsequent) sulfur abstraction.

In order to gain insight into the formation of dithiocarbonimidato or diphenylsilyl complexes, we further examined the chemical reactivity of organic isothiocyanates toward other Pd compounds of tertiary phosphines. We have already reported that reactions of trans-[PdEt$_2$L$_2$] with H$_2$SiPh$_2$ gave the silyl-bridged dinuclear Pd complexes [Pd(μ-HSiPh$_2$)L]$_2$ (L = PMe$_3$, etc.) [35,36]. So, we could not use such dinuclear silyl complexes for our study because it may cause a different reactivity toward organic isothiocyanates. Instead, we tried to examine direct reactions of diethyl Pd(II) complexes with isothiocyanates. Trans-[PdEt$_2$L$_2$] (L = PMe$_3$, PMe$_2$Ph) were treated directly with 2 equiv or excess R—NCS at room temperature, and the corresponding dithiocarbonimidato Pd(II) complexes could be obtained in 49–90% yields (Eq. (4)). Similar reactions employing [Pd(styrene)L$_2$], which is

generated in situ from trans-[PdEt$_2$L$_2$] and styrene, gave also the same Pd compounds. All products were characterized by spectroscopic data and elemental analyses. The IR spectra of **4**–**6** display a strong C=N band at 1552–1566 cm^{-1} due to the dithiocarbonimidato group (S$_2$C= N—R). The ^{31}P NMR data of **4**–**6** show two doublets due to two

$$\text{(4)}$$

4 (L = PMe$_3$, R = Ph)
5 (L = PMe$_3$, R = Et)
6 (L = PMe$_2$Ph, R = Ph)
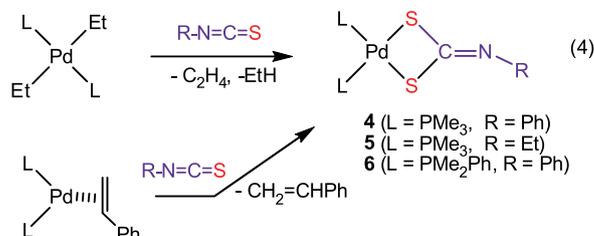
magnetically inequivalent PR$_3$ ligands. Molecular structures of **4** and **6** have been determined by X-ray diffraction.

The π-coordination of R—NCS into the low-valent Rh(I) [34] or Co (0) [37] species and subsequent dimerizaion to form the five-membered metallacycle intermediates, which ultimately go to the dithiocarbonimidato complexes had previously been proposed. On the basis of Eqs. (1), (2) and (4) and the foregoing proposition, we speculate that the starting complex [Pd(SiHPh$_2$)$_2$L$_2$] first undergoes reductive elimination of Ph$_2$HSi—SiHPh$_2$ or α-elimination of H$_2$SiPh$_2$ to generate the Pd(0) compound, which reacts with R—NCS to form the π-coordinated intermediate [Pd(R—NCS)L$_2$] (Scheme 1). This intermediate reacts further with another R—NCS to give the second intermediate, from which isocyanide (R—NC) liberates to give the ultimate product. This speculation may explain the formal S=C bond cleavage in R—NCS during the reaction. In the reaction mixtures in Eqs. (1) and (2), we observed the characteristic signals assignable to the isocyanide (R-NC) and H$_2$SiPh$_2$ by IR spectroscopy or GC—mass spectrometry, which are believed to be due the liberated organic products during the reactions. However, we could not detect Ph$_2$HSi—SiHPh$_2$ in Eqs. (1) and (2) in the NMR and MS spectra of the reaction mixtures. In contrast, the presence of Ph$_2$HSi—SiHPh$_2$ in Eq. (3) could be confirmed by mass spectrometry (ESI-TOF).

The crystal and refinement data of **2**–**4** and **6** are summarized in Table 1. Fig. 1 shows the molecular structure of cis-[Pd(S$_2$SiPh$_2$) (dmpe)] (**2**), which shows a slightly distorted square-planar coordination, consisting of two PMe$_2$ groups and two bridging sulfide (μ—S) ligands that are linked to the SiPh$_2$. The Pd—S bond lengths (2.378(6) and 2.391(6) Å) in **2** are close to those (2.362(1) and 2.392 (1) Å) in [Pd(S$_2$SiMe$_2$)(PEt$_3$)$_2$] [38,39], which was prepared from [Pd (OAc)]$_2$ and (SSiMe$_2$)$_3$. These bond lengths are comparable to the Pt—S bond lengths in [Pt(S$_2$SiPh$_2$)(PEt$_3$)$_2$] (2.392(1) Å) [29], [Pt (S$_2$SiPh$_2$)(PMe$_2$Ph)$_2$] (2.376(1) Å) [29], and [Pt(S$_2$Si(Tbt)(Mes) (PPh$_3$)$_2$] (Tbt = 2,4,6-tris[bis(trimethylsilyl)]methyl]phenyl) (2.367 (15) and 2.333(17) Å) [40]. These data indicate that the dithiolato—Pd (II) complexes are less symmetric (different M—S bond lengths) than the Pt(II) complexes having a bridged silane group, reflecting more distorted metallacyclobutane rings containing diphenylsilyl group in the former than those in the latter ones. Interestingly, the Pd1···Si separation (2.9887(6) Å) is much less shorter the sum of van der
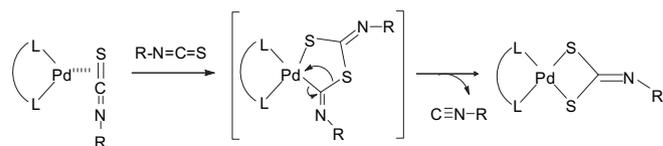
Scheme 1.

Table 1
X-ray data collection and structure refinement for **2**–**4** and **6**.

	2	**3**	**4**	**6**
Formula	$C_{18}H_{26}P_2PdS_2Si$	$C_{10}H_{21}NP_2PdS$	$C_{13}H_{23}NP_2PdS_2$	$C_{23}H_{27}NP_2PdS_2$
fw	502.94	355.68	425.78	549.92
Temperature, K	296(2)	296(2)	296(2)	296(2)
Crystal size (mm³)				
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic
Space group	$Pna2_1$	$P2_12_12_1$	$P2_12_12_1$	$P1$
a, Å	16.0226(14)	9.1802(2)	9.8909(1)	9.7110(2)
b, Å	15.5152(14)	9.5367(2)	10.1830(1)	9.9037(2)
c, Å	8.8319(8)	17.1700(4)	18.0201(2)	13.2588(2)
α, deg	90	90	90	106.599(1)
β, deg	90	90	90	95.102(1)
γ, deg	90	90	90	91.354(1)
V, Å³	2195.6 (3)	1503.21(6)	1814.97(3)	1215.57(4)
Z	4	4	4	2
d_{cal}, g cm⁻³	1.522	1.572	1.558	1.502
μ, mm⁻¹	0.235	1.559	1.417	1.077
$F(000)$	1024	720	864	560
T_{min}	0.7083	0.5743	0.8484	0.7821
T_{max}	0.8461	0.6192	0.8951	0.8816
No. of reflns measured	53,702	30,978	21,186	10,397
No. of reflns unique	5389	3703	4479	5921
No. of reflns with $I > 2\sigma(I)$	4869	3499	3980	5069
No. of params refined	218	220	173	262
Max. in $\Delta\rho$ (e Å⁻³)	0.348	0.409	0.454	0.369
Min. in $\Delta\rho$ (e Å⁻³)	−0.169	−0.433	−0.319	−0.301
GOF on F^2	1.035	1.059	1.024	1.024
$R1^a$	0.0204	0.0184	0.0294	0.0269
$wR2^b$	0.0423	0.0461	0.0558	0.0598

[a] $R1 = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$.
[b] $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

Waals radii of Pd (1.63 Å) and Si (2.10 Å) atoms, indicating a very strong van der Waals contact or an elongated Pd–Si bond.

The ORTEP drawing of $[(\eta^3\text{-allyl})Pd(dmpe)](NCS)$ (**3**) in Fig. 2 clearly reveals a square plane consisting of a chelating phosphine (dmpe) and a π-allyl fragment around the Pd center. On the other hand, Figs. 3 and 4 show the molecular structure of dithiocarbonimidato Pd(II) complexes (**4** and **6**), whose Pd–S bond lengths (2.314(7)–2.344(7) Å) are similar to those (2.310(5)–2.343(1) Å) observed for other dithiocarbonimidato Pd(II) complexes, [Pd(S₂CN–CH₂Ph)(PEt₃)₂] [41,42] and [Pd(S₂CNCOOEt)(PPh₃)₂] [30].

In summary, we carried out several reactions of the bis(silyl) Pd(II) complex [Pd(SiHPh₂)₂(dmpe)] with organic isothiocyanates.

These reactions gave the novel dithiocarbonimidato Pd(II) complex [(PdS₂C=NPh)(dmpe)], the diphenylsilanedithiolato Pd(II) complex [Pd(S₂SiPh₂)(dmpe)], and a π-allyl complex [(η^3-allyl)Pd(dmpe)](NCS) by sulfur abstraction from organic isothiocyanates and the silyl elimination. We alternatively prepared dithiocarbonimidato complexes, [Pd(S₂C=N–R)L₂].

3. Experimental

General Methods. All manipulations of air-sensitive compounds were performed under N₂ or Ar by standard Schlenk-line techniques. Solvents were distilled from Na-benzophenone. Analytical
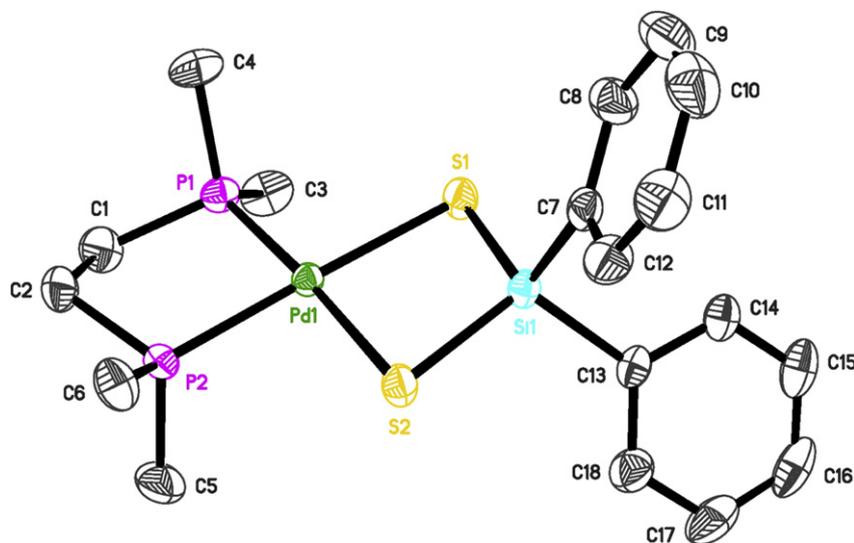
Fig. 1. *ORTEP* drawing of **2** showing the atom-labeling scheme and 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Pd1–P2 2.2405(6), Pd1–P1 2.2473 (6), Pd1–S2 2.3775(6), Pd1–S1 2.3961(6), S1–Si1 2.1041(8), S2–Si1 2.1005(8); P2–Pd1–P1 85.52(2), P2–Pd1–S2 90.79(2), P1–Pd1–S2 176.29(2), S2–Pd1–S1 88.48(2), S i1–S1–Pd1 82.96(2), Si1–S2–Pd1 83.49(2).
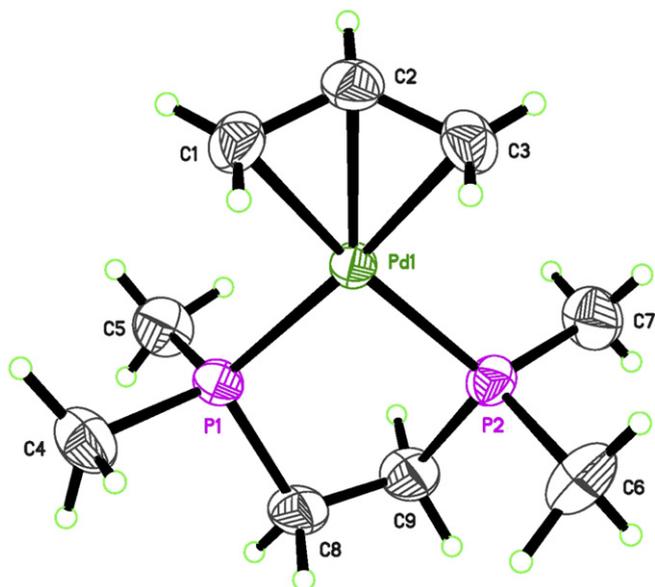
Fig. 2. *ORTEP* drawing of **3**. Selected bond lengths (Å) and angles (°): Pd1–C2 2.149(2), Pd1–C3 2.171(2), Pd1–C1 2.183(2), C1–C2 1.384(4), C2–C3 1.386(4), Pd1–P2 2.2761(6), Pd1–P1 2.2768(5); C3–Pd1–C1 67.53(10), P2–Pd1–P1 87.31(2), N1–C10–S1 177.3(9).

laboratory at Kangneung-WonJu National University carried out elemental analyses. IR spectra were recorded on a Perkin Elmer BX spectrophotometer. GC-MS was performed on a Agilent 6890 GC/5973i MSD. Exact mass was measured on a ESI-TOF API QSTAR Pulsar I. NMR (^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H}) spectra were obtained on JEOL Lamda 300 MHz spectrometer. Chemical shifts were referenced to internal Me$_4$Si (^{1}H and ^{13}C{^{1}H}) or external 85% H$_3$PO$_4$ (^{31}P{^{1}H}). Ph–NCS, CH$_2$=CHCH$_2$NCS, and ^{i}Pr–NCS were purchased. [Pd(SiHPh$_2$)$_2$L$_2$] (L$_2$ = dmpe) [43] and *trans*-PdEt$_2$L$_2$ (L = PMe$_3$, PMe$_2$Ph) [44,45] were prepared by the literature methods.

3.1. Preparation of complexes *1* and *2*

To a Schlenk flask containing [Pd (SiHPh$_2$)$_2$(dmpe)] (0.435 g, 0.697 mmol) was added THF (4 ml) and Ph–NCS (0.189 g, 1.39 mmol). After stirring for 6 h at 50 °C, the resulting orange

solution was completely evaporated under vacuum, and then the oily residue was solidified with *n*-hexane. The solids were filtered and washed with hexane (2 × 2 ml). Recrystallization from ether/CH$_2$Cl$_2$ (3:1) gave white crystals of [Pd(S$_2$C=N–Ph)(dmpe)], (1, 0.227 g, 77%). IR (KBr, cm^{-1}): ν(CN) 1553. ^{1}H NMR (DMSO-d^6, δ): 1.57 (dd, J = 11, 19 Hz, 12H, PMe$_2$), 2.07 (d, J = 19 Hz, 4H, P-CH$_2$), 6.80–6.83 (m, 3H, Ph), 6.89–6.94 (m, 2H, Ph). ^{13}C{^{1}H} NMR (DMSO-d^6, δ): 11.1 (d, J$_{P-C}$ = 25 Hz, PMe$_2$), 26.9 (dd, J$_{P-C}$ = 15, 32 Hz, PCH$_2$), 121.9, 128.2, 148.3, 179.2 (CN). ^{31}P{^{1}H} NMR (DMSO-d^6, δ): 40.1 (d, J = 36 Hz), 40.8 (d, J = 36 Hz). *Anal.* Calcd for C$_{13}$H$_{21}$NP$_2$S$_2$Pd: C, 36.84; H, 4.99; N, 3.30. Found: C, 36.84; H, 5.18; N, 2.99.

The collected filtrates were analyzed by IR spectroscopy and GC–mass spectrometry. Their IR spectra show the characteristic bands assignable to the C≡N bond in isocyanide at 2164 cm^{-1} and the Si–H bond in H$_2$SiPh$_2$ at 2102 cm^{-1}. MS: 103 (M$^+$) (for C≡N–Ph) and 184 (M$^+$) (for H$_2$SiPh$_2$).

To a Schlenk flask containing [Pd(SiHPh$_2$)$_2$(dmpe)] (0.351 g, 0.563 mmol) was added THF (4 ml) and ^{i}Pr–NCS (0.114 g, 1.13 mmol) at room temperature. The reaction mixture was stirred for 16 h to give a yellow precipitate. The solids were filtered and washed with hexane (2 × 2 ml) (0.166 g, 59%). Recrystallization of [Pd(S$_2$SiPh$_2$)(dmpe)] (2) from ether/CH$_2$Cl$_2$ (3:1) gave white crystals suitable for X-ray diffraction study. ^{1}H NMR (DMSO-d^6, δ): 1.61 (d, J = 12 Hz, 12H, PMe$_2$), 2.04 (d, J = 20 Hz, 4H, P-CH$_2$), 7.25–7.30 (m, 6H, Ph), 7.58–7.62 (m, 4H, Ph). ^{13}C{^{1}H} NMR (DMSO-d^6, δ): 12.9 (dt, J$_{P-C}$ = 7.4, 28 Hz, PMe$_2$), 26.9 (dd, J$_{P-C}$ = 22 Hz, PCH$_2$), 126.9, 128.0, 132.9, 145.8. ^{31}P{^{1}H} NMR (DMSO-d^6, δ): 47.6. *Anal.* Calcd for C$_{18}$H$_{26}$P$_2$S$_2$SiPd: C, 42.98; H, 5.21; S, 12.75. Found: C, 42.63; H, 5.51; S, 12.29.

Ph$_2$SiHSiHPh$_2$: MS (ESI-TOF) Calcd for C$_{24}$H$_{22}$Si$_2$ (M + H)$^+$: 367.1338. Found for 367.2867

3.2. Preparation of the complex *3*

At room temperature, THF (5 ml) and CH$_2$=CHCH$_2$NCS (0.105 g, 1.06 mmol) were added to [Pd(SiHPh$_2$)$_2$(dmpe)] (0.331 g, 0.53 mmol). The reaction mixture was stirred overnight to give a yellow precipitate. The resulting solids were filtered and washed with hexane (2 × 2 ml). The filtrate was completely evaporated under vacuum, and then the oily residue was solidified with *n*-hexane. The collected solids were recrystallized from *n*-hexane/
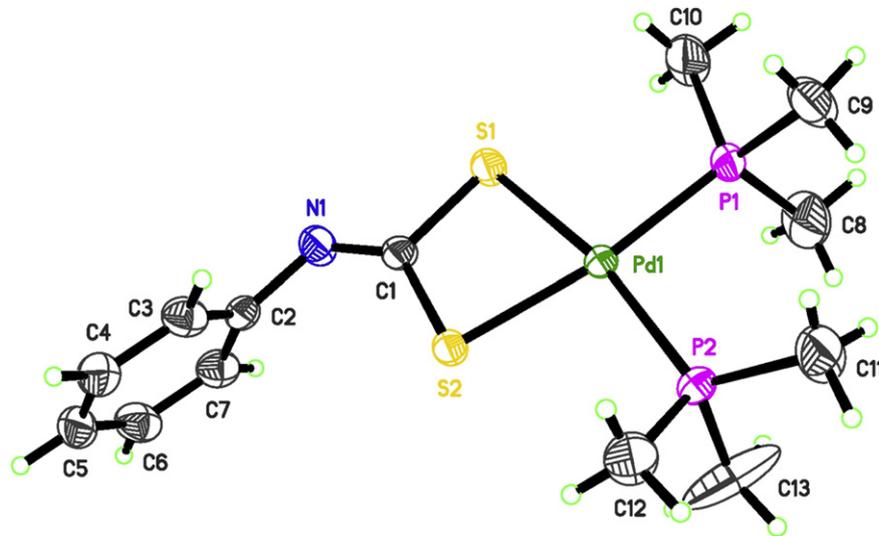
Fig. 3. *ORTEP* drawing of **4**. Selected bond lengths (Å) and angles (°): Pd1–P1 2.2915(7), Pd1–P2 2.2959(8), Pd1–S1 2.3143(7), Pd1–S2 2.3440(7), S1–C1 1.758(3), S2–C1 1.762(3), N1–C1 1.261(4), N1–C2 1.418(4); P1–Pd1–P2 97.49(3), P1–Pd1–S1 92.95(3), P2–Pd1–S2 93.90(3), S1–Pd1–S2 75.50(3), C1–S1–Pd1 88.61(9), C1–S2–Pd1 87.59(9), C1–N1–C2 123.1(3), N1–C1–S1 121.6(2), N1–C1–S2 130.1(2), S1–C1–S2 108.23(15).
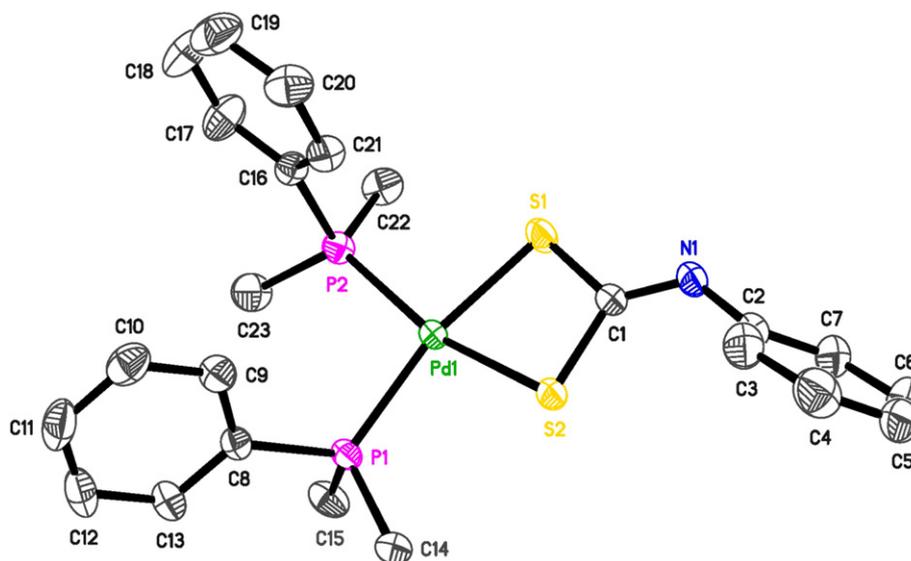
Fig. 4. *ORTEP* drawing of **6**. Selected bond lengths (Å) and angles (°): Pd1–P1 2.2922(5), Pd1–P2 2.2996(6), Pd1–S1 2.3197(6), Pd1–S2 2.3335(5), S1–C1 1.752(2), S2–C1 1.765(2); P1–Pd1–P2 98.27(2), P1–Pd1–S1 168.26(2), P2–Pd1–S1 92.05(2), P1–Pd1–S2 94.93(2), P2–Pd1–S2 165.21(2), S1–Pd1–S2 75.55(2), C1–S1–Pd1 88.45(7), C1–S2–Pd1 87.71(7), N1–C1–S1 121.4(2), N1–C1–S2 130.3(2), S1–C1–S2 108.3(1).

CH_2Cl_2 (5:1) to form white crystals of complex **3** (0.189 g, 58%). IR (KBr, cm^{-1}): ν(NCS) 2054. ^1H NMR (CDCl$_3$, δ): 1.78 (m, 12H, P*Me$_2$*), 2.12 (d, *J* = 17 Hz, 4H, PC*H$_2$*), 3.78(br, 4H, C*H$_2$*), 6.38 (qnt, *J* = 11H, 1H, C*H*). $^{13}C\{^1H\}$ NMR (CDCl$_3$): 15.3 (dt, *J*$_{P-C}$ = 12, 126 Hz, P*Me$_2$*), 28.8 (dd, *J*$_{P-C}$ = 22, 24 Hz, PC*H$_2$*), 66.0 (t, *J*$_{P-C}$ = 17 Hz, *CH$_2$*), 121.6 (t, *J*$_{P-C}$ = 5.9 Hz, *C*H). $^{31}P\{^1H\}$ NMR (CDCl$_3$): 29.7(s). *Anal.* Calcd for C$_{10}$H$_{19}$NP$_2$SPd: C, 33.76; H, 5.95; N, 3.94. Found: C, 33.94; H, 6.05; N, 3.67.

3.3. Preparation of complexes 4–6

These complexes were prepared in the same way. To a Schlenk flask containing *trans*-PdEt$_2$(PMe$_3$)$_2$ (0.458 g, 1.45 mmol) was added Ph–NCS (0.391 g, 2.89 mmol) and THF (4 ml). The reaction mixture was stirred overnight at room temperature to give yellow precipitates, which were filtered and washed with hexane (2 × 2 ml). Recrystallization from *n*-hexane/CH$_2$Cl$_2$ (3:1) gave white crystals of complex **4** (0.303 g, 49%). IR (KBr, cm^{-1}): ν(CN) 1563. ^1H NMR (CDCl$_3$, δ): 1.48 (d, *J* = 9.5, 9H, P*Me$_3$*), 1.54 (d, *J* = 9.5, 9H, P*Me$_3$*), 6.98–7.04 (m, 1H, Ph), 7.08–7.11 (m, 2H, Ph). 7.23–7.29 (m, 2H, Ph). $^{13}C\{^1H\}$ NMR (CDCl$_3$): 16.2 (ddd, *J*$_{P-C}$ = 6.5, 16 Hz, P*Me$_3$*), 122.2, 122.9, 128.3, 147.5, 175.8 (CN). $^{31}P\{^1H\}$ NMR (CDCl$_3$): −16.2(d, *J* = 51 Hz), −16.7 (d, *J* = 51 Hz). *Anal.* Calcd for C$_{13}$H$_{23}$NP$_2$S$_2$Pd: C, 36.67; H, 5.44; N, 3.29. Found: C, 36.64; H, 5.65; N, 3.26.

Data for [Pd(S$_2$C=N–Et)(PMe$_3$)$_2$], (5, 57%). IR (KBr, cm^{-1}): ν(CN) 1566. ^1H NMR (CDCl$_3$, δ): 1.25 (t, *J* = 7.1 Hz, 3H, C*H$_3$*), 1.53 (d, *J* = 9.0 Hz, 18H, P*Me$_3$*), 3.66 (q, *J* = 7.3 Hz, 2H, C*H$_2$*), 6.98–7.04 (m, 1H, Ph), 7.08–7.11 (m, 2H, Ph). 7.23–7.29 (m, 2H, Ph). $^{13}C\{^1H\}$ NMR (CDCl$_3$): 16.2 (ddd, *J*$_{P-C}$ = 5.0, 13 Hz, P*Me$_3$*), 15.8 (s, C*H$_3$*), 42.2 (s, C*H$_2$*), 171.0 (s, CN). $^{31}P\{^1H\}$ NMR (CDCl$_3$): −16.6 (d, *J* = 51 Hz), −17.3 (d, *J* = 51 Hz). *Anal.* Calcd for C$_9$H$_{23}$NP$_2$S$_2$Pd: C, 28.61; H, 6.13; N, 3.71. Found: C, 28.83; H, 6.41; N, 3.30.

Data for [Pd(S$_2$C=N–Ph)(PMe$_2$Ph)$_2$], (6, 90%). IR (KBr, cm^{-1}): ν (CN) 1552. ^1H NMR (CDCl$_3$, δ): 1.41 (d, *J* = 9.3 Hz, 6H, P*Me$_2$*), 1.48 (d, *J* = 9.3 Hz, 6H, P*Me$_2$*), 7.00–7.06 (m, 1H, Ph), 7.15–7.19 (m, 2H, Ph). 7.26–7.45 (m, 2H, Ph). $^{13}C\{^1H\}$ NMR (CDCl$_3$): 14.0 (ddd, *J*$_{P-C}$ = 5.0, 20 Hz, P*Me$_2$*), 122.3, 122.9, 128.3, 128.7, 128.8, 128.9, 129.0, 130.5, 130.6, 133.3, 147.4, 175.8 (s, CN). $^{31}P\{^1H\}$ NMR (CDCl$_3$): −6.89 (d, *J* = 49 Hz), −7.49 (d, *J* = 49 Hz). *Anal.* Calcd for C$_{23}$H$_{27}$NP$_2$S$_2$Pd: C, 48.98; H, 4.83; N, 4.97. Found: C, 49.07; H, 4.92; N, 4.87.

Complex **4** was prepared in another way. To a Schlenk flask containing *trans*-PdEt$_2$(PMe$_3$)$_2$ (0.278 g, 0.878 mmol) at 0 °C were added sequentially styrene (0.274 g, 2.63 mmol) and THF (2 ml). The mixture was heated at 55 °C for 1 h to give a yellow solution. At room temperature, on addition of Ph–NCS (0.119 g, 0.878 mmol) to the mixture, the yellow solution turned to an orange one. After stirring for 16 h at room temperature, the solvent was completely removed under vacuum, and then the resulting residue was solidified with *n*-hexane. The resulting white solids were filtered, washed with *n*-hexane (2 × 2 ml) and dried under vacuum to give **4** (0.426 g, 59%). Complexes **5** and **6** were analogously prepared.

Complexes **4** and **6** were also independently prepared from the reactions of PdL$_4$ (L = PMe$_3$, PMe$_2$Ph) with Ph–NCS [31].

3.4. X-ray structure determination

All X-ray data were collected with a Bruker Smart APEX2 diffractometer equipped with a Mo X-ray tube. Collected data were corrected for absorption with SADABS based upon the Laue symmetry by using equivalent reflections [46]. All calculations were carried out with SHELXTL programs [47]. All structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were generated in ideal positions and refined in a riding model.

Acknowledgment

Appendix A. Supplementary data

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