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Complexation of *N*-heterocyclic silylenes to Pd(0): formation of highly labile homoleptic complexes Pd[Si(^{t}BuNCH$_2$CH$_2$N^{t}Bu)]$_4$ and Pd[Si(^{t}BuNCHCHN^{t}Bu)]$_3$

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Abstract

The reaction of *N*-heterocyclic silylenes (NHS) **1** and **2** with Pd complexes, notably [(*tert*-butyl)$_3$P]$_2$Pd(0) and (COD)Pd(CH$_3$)$_2$, is described. The formation of homoleptic NHS complexes Pd[Si(^{t}BuNCH$_2$CH$_2$N^{t}Bu)]$_4$ and Pd[Si(^{t}BuNCHCHN^{t}Bu)]$_3$ is reported. The rearrangement of these complexes into dinuclear silylene-bridged compounds and the solid state structures of the latter complexes are discussed. © 2002 Published by Elsevier Science B.V.

Keywords: *N*-heterocyclic silylenes; Pd complexes; μ-Silylene complexes; X-ray structures

1. Introduction

N-heterocyclic carbenes have proven to be a versatile and important class of ligands both in coordination chemistry and homogeneous catalysis [1–3]. The main characteristic of these ligands is to act as a strong donor, which even surpasses that of phosphine ligands. In this respect, homologous *N*-heterocyclic silylenes promise to exhibit a further enhancement of the donor ability. Continuing our investigations on the catalytic performance of Pd(0) complexes containing *N*-heterocyclic carbenes, we therefore studied the complexation behavior of *N*-heterocyclic silylenes toward late transition metals. Whereas silylene **2** has been investigated in greater detail in recent years, notably by West et al. [4] and Tilley and co-workers [5], there is only little known about the coordination chemistry of the saturated analog **1** [6]. In this paper, we present the synthesis of the first homoleptic Pd complexes of NHS **1** and **2** as well as their rearrangement reactions to dinuclear silyl-bridged species[1]. Complex **7** was reported briefly in a recent review article [2].

2. Results and discussion

2.1. Reaction of saturated silylene **1** with Pd(P^{t}Bu$_3$)

Bis(tri-*tert*-butyl)phosphinepalladium(0) **3** reacts with *N*-heterocyclic carbenes with formation of the homoleptic carbene complex **4** [7]. In a similar reaction, **3** is treated with silylene **1** [8]. As evidenced by ^{31}P-NMR, on employing a 1:2 Pd/Si stoichiometry, the formation of free phosphine can be detected. Surprisingly, the starting complex **3** is not fully consumed even after prolonged reaction times, although a complete complexation of the silylene is detected in the ^{1}H-NMR as well as in the ^{29}Si-NMR spectrum. Additionally, the ^{31}P-NMR spectrum exhibits only the signals of the starting complex and free phosphine. When the Si/Pd ratio is 4:1 or higher, a complete elimination of tri(*tert*-

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[1] While this paper was in print, a dinuclear palladium complex exhibiting related μ-silylene ligands was reported [23].

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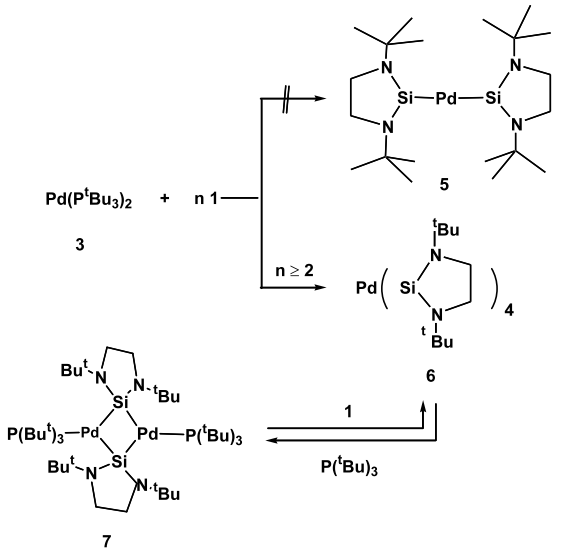


Scheme 1.

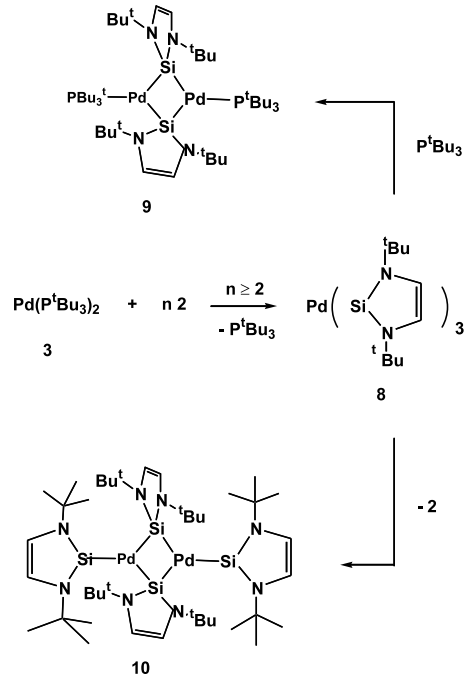
butyl)phosphine is detected. The ^{31}P-NMR and ^{29}Si-NMR spectra, in combination, indicate the formation of homoleptic complex **6** as the only product (Scheme 1).

Reaction of $(COD)_2Ni$ with saturated silylene **1** is known to give $Ni[Si(^tBuNCH_2CH_2N^tBu)]_3$ [9]. In contrast, the compound formed here consists of four silylene ligands and one Pd atom, as evidenced by NMR data. By transferring these findings into a preparative scale, the reaction sequence is widened by another complex being formed during the course of the work up. It appeared that it was not possible to isolate the homoleptic species since upon concentrating the reaction solution, tri-*tert*-butylphosphine again reacts with complex **6**. But instead of its reaction back to the starting compound **3**, a new complex is formed from the solution, which shows one signal for coordinated phosphine ($\delta = 93.36$ ppm) in the ^{31}P-NMR spectrum and only one set of signals characteristic of the silylene ligand. A ^{29}Si-NMR spectrum could not be recorded due to the low solubility of the complex. A crystal structure determination (vide infra) reveals complex **7**, in fact, to be dinuclear, with a linear arrangement of the P–Pd–Pd–P chain and two silylene ligands bridging the Pd–Pd bond. Such μ-silylene complexation is known from activation of silanes by, for example, platinum. In such cases, the low-valent metal adds oxidatively to the Si–H bond, thus forming one or more μ-silylene ligands [10]. Very recently, Fürstner et al. reported a compound analogous to **7**, with a bridging unsaturated silylene **2** and triphenylphosphine as the phosphine ligand [23]. Upon treating **7** with silylene **1**, a slow reaction occurs during which the phosphine is released completely, leading to complex **6**. But a quantitative back reaction to complex **6** can only be accomplished when a large excess of free silylene is used. Since the presence of noncoordinated phosphine obviously inhibits the isolation of the homoleptic complex **6**, we were seeking for a phosphine-free synthetic route to this compound. As mentioned above, $Ni(COD)_2$ had been used successfully to form homoleptic Ni–silylene complexes. Since the corresponding Pd complex is thermally very labile, its reaction with **1** results in complicated mixtures where the compounds described above could be detected only in small amounts.

2.2. Reaction of unsaturated silylene **2** with $Pd(P^tBu_3)_2$

In the chemsitry of *N*-heterocyclic carbenes, the unsaturated carbenes show distinct differences in their coordination toward metals as well as in influencing the catalytic performance of corresponding complexes in homogeneous catalysis [1,2,11]. It was therefore worthwhile to compare both saturated and unsaturated *N*-heterocyclic silylenes **1** and **2**. On treating complex **3** with **2** under the same conditions as described above, a similarly complicated reaction pattern occurred. With a large excess of silylene, again a homoleptic Pd–silylene complex **8** is formed, although this time, only a Pd/Si ratio of 1:3 could be established. The reason for this behavior is not yet clear, but it corresponds well with the coordination of the silylene found in the Ni complexes mentioned above. Interestingly, Lappert and coworkers reported that four molecules of silylene $Si[(^tBuCH_2N)_2\text{-}1,2\text{-}C_6H_4]$ coordinate to one Ni(0) atom [12]. A smaller steric effect of the neopentyl substituents can be regarded as the reason for the different stoichiometries in the Ni complexes. But steric reasons are not obvious for the differences between the two Pd complexes, **6** and **8**. As in the case of the saturated silylene, complex **8** is not stable in the presence of phosphine so that during work up, the corresponding dinuclear complex **9** crystallizes from the reaction solution (Scheme 2).

If a Pd/Si ratio of 1:2 is used, complex **8** is again formed as the main product after a few minutes. Upon reaction for a prolonged time, complex **8** vanishes, and a new homoleptic complex forms, as shown in the ^{1}H-NMR spectrum. The ring protons of the silylene ligand **2** are found at $\delta = 6.70$ ppm. After a few minutes, this signal decreases, and two new signals at $\delta = 6.87$ and 6.61 ppm become prominent (Fig. 1). Additionally, the appearance of a signal for free phosphine in the ^{31}P-NMR spectrum indicates a phosphine-free new complex. This and the fact that in the ^{29}Si-NMR spectrum, two different Si signals at $\delta =$ 106.6 and 107.9 ppm were found, agree well with the presence of a dinuclear complex analogous to complex **9** but having terminal and bridging silylene ligands instead. Not surprisingly, this compound **10** cannot be isolated from these reaction mixtures since the still-present phosphine eventually leads to the mixed dinu-



Scheme 2.

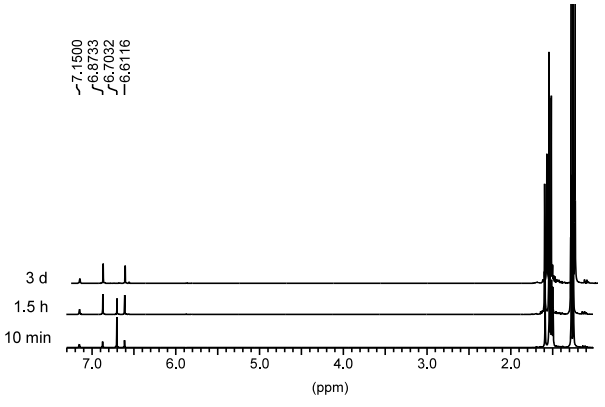
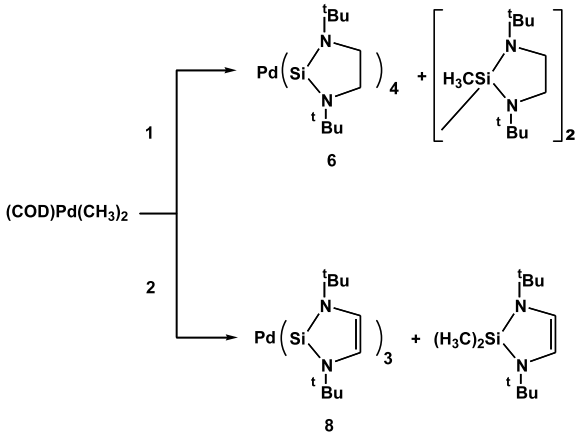


Fig. 1. ^{1}H-NMR spectrum (benzene-d_8 solution) of compound **8** at $t = 10$ min, 1.5 h, 3 days.



Scheme 3.

clear complex **9**. Unfortunately, treatment of **2** with Pd(COD)$_2$ at low temperature does, again, not provide the desired product **8**. This can be achieved by reaction of the more stable complex Pd(COD)(CH$_3$)$_2$ with four equivalents of silylene **2** (Scheme 3).

During the course of the reaction, one silylene **2** molecule is consumed by reducing Pd(II) to Pd(0), while concomitantly taking up the two methyl groups and forming (CH$_3$)$_2$Si('BuNCHCHN'Bu) (**11**) [13]. COD and **11** are removed during solvent evaporation, leaving behind pure complex **8**. Once isolated, it was possible to study the chemistry of **8** in more detail. It turned out that an equilibrium is established between **10**, **2** and **8** (Fig. 2). At the beginning, one signal for the ring protons of the silylene ligand ($\delta = 6.71$) and tiny signals for free silylene **2** ($\delta = 6.75$) and **10** ($\delta = 6.88$, 6.62) are seen. Within 3 days, the signals for **10** and free NHS **2** grow.

Since, as mentioned above, it was not possible to isolate pure complex **6**, saturated silylene **1** was also treated with Pd(COD)(CH$_3$)$_2$ (Scheme 3). In this case, two silylenes are consumed to bring about the reduction of Pd(II) and the formation of disilane **12** [14], which consists of two CH$_3$Si('BuNCH$_2$CH$_2$N'Bu) entities. The only Pd-containing is complex **6**, which forms quantitatively. Unfortunately, upon removal of the solvent, saturated silylene **1** is liberated and Pd-black forms eventually. This reaction shows that silylene **1** is able to act as a one-electron reducing agent, thus being possibly liable to radical chemistry.

2.3. Structure determination of 7 and 9

Single crystals of complexes **7** and **9** could be obtained from benzene solutions by slow evaporation of the solvent. Selected bond lengths and angles are displayed in Table 1.

The molecular structures of both complexes in the solid state, as shown in Figs. 3 and 4, consist of a linear chain of P–Pd–Pd–P atoms (Pd–Pd–P angle **7**: 179.06(1)°, **9**: 179.74(1)°), being bridged by two silylene units, where the NHS are placed perpendicular to the Pd–Pd axis. The Pd–Pd distance is shorter in complex **7** (**7**: 267.79(2) pm, **9**: 270.70(2) pm) but both distances are slightly longer than in dinuclear Pd(I) complexes of comparable structure (Pd–Pd 253–270 pm) [15] but shorter than in Pd metal (275 pm). This corresponds to a decrease in the bridging angle Pd–Si–Pd for **7** (**7**: 67.04(1)°, **9**: 68.49(1)°). Structures with bis-silylene bridges are quite common in silicon chemistry [16]. In comparable cases, the corresponding M–Si–M angles are found to be in the range of 70°. These data have to be compared with those of a closely related analog of compound **9** reported very recently by Fürstner et al. [23]. In this complex, triphenylphosphine is coordinated

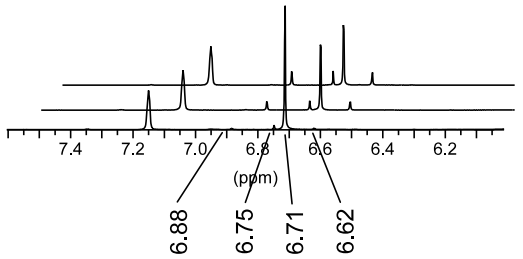


Fig. 2. ^{1}H-NMR spectrum (benzene-d_8 solution) of compound **8** at $t = 0$ h, 1.5 days, 3 days.

Table 1
Selected bond lengths (pm) and bond angles (°) for compounds **7** and **9**

	7	**9**
Bond lengths		
Pd–Pd_a	267.79(2)	270.70(2)
Pd–Si	239.43(6)	237.62(5)
Pd–Si_a	245.43(5)	243.35(5)
Pd–P	236.32(5)	237.46(5)
Si–N1	174.16(19)	176.33(15)
Si–N2	174.02(18)	177.10(19)
N1–C1	145.2(3)	138.1(3)
N1–C3	147.3(3)	148.7(3)
N2–C2	147.5(11)	138.1(3)
N2–C7	147.0(3)	148.5(3)
Bond angles		
Pd–Si–Pd_a	67.04(1)	68.49(1)
Pd_a–Pd–P	179.06(1)	179.74(1)
Si_a–Pd–P	123.70(2)	125.04(2)
Si–Pd–P	123.34(2)	123.45(2)
Si–Pd–Si_a	112.96(2)	111.51(2)
Pd_a–Pd–Si	57.55(1)	56.76(1)
Pd_a–Pd–Si_a	55.41(1)	54.75(1)
N1–Si–N2	91.34(8)	88.75(8)

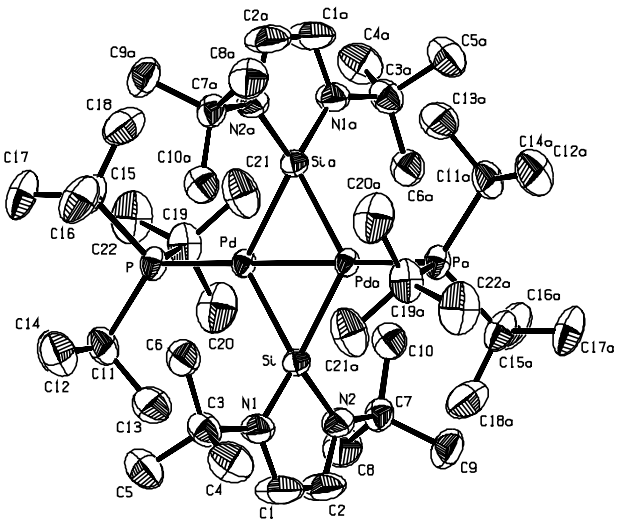


Fig. 3. ORTEP plot of complex **7** (without hydrogen atoms).

to the Pd atoms instead of tri(*tert*-butyl)phosphine. The phosphine exchange results in a shortening of the Pd–Pd distance to 265.005 pm, which is even shorter than that found in complex **7**. Accordingly, further diminishing of the Pd–Si–Pd angle to 66.78° is observed in the triphenylphosphine derivative. The different electronic behavior of the triphenylphosphine compared to tri(*tert*-butyl)phosphine is reflected by the Pd–P bond lengths. Whereas the Pd–P bond length in compounds **7** and **9** is 236.32(5) and 237.46(5) pm, respectively, it is shortened by 10 pm in Fürstner's compound (227.06 pm). Comparison of complex **7** with **9** and with its triphenylphosphine analog also shows that some degree of asymmetry is present in the build up of the Pd–Si–Pd–Si core. In complexes **7** and **9**, a significant difference in the Pd–Si and Pd–Si_a is found, which slightly corresponds to a formulation of the molecule as a dimer of the elusive mixed complex, (silylene)-Pd(phosphine). This asymmetry is diminished when triphenylphosphine, as a better acceptor ligand, is present.

3. Conclusions

We have shown that *N*-heterocyclic silylenes **1** and **2** can be coordinated successfully to Pd(0). The coordination chemistry differs significantly from that of *N*-heterocyclic carbenes. In the first step, homoleptic silylene complexes are formed, with different Pd/Si ratios. Similar to Pd–phosphine complexes, these complexes are labile. But contrary to Pd–phosphine and Pd–NHC complexes, they can rearrange to dinuclear species, which in the presence of phosphines can even be isolated. Fürstner et al. have very recently described the use of dinuclear μ-silylene complexes of the kind analogous to compounds **7** and **9** in Suzuki-type coupling reactions of bromo-arenes [23]. In the light of the reactions described here, it seems quite possible that these dinuclear complexes are not the active catalysts but are the 'dormant state' stabilizing the catalyst against decomposition to palladium-black precipitation. Additionally, comparison with Pt complexes isolated in mechanistic studies of hydrosilylation [17] show that these dinuclear compounds described here could possibly be active in hydrogenation reactions. Investigations in this direction and on the mechanism and use of these complexes in Pd-catalyzed C–C coupling reactions are under way.

4. Experimental

All manipulations were carried out under Argon, using standard Schlenk techniques or an argon-filled glovebox. Solvents were dried prior to use and de-

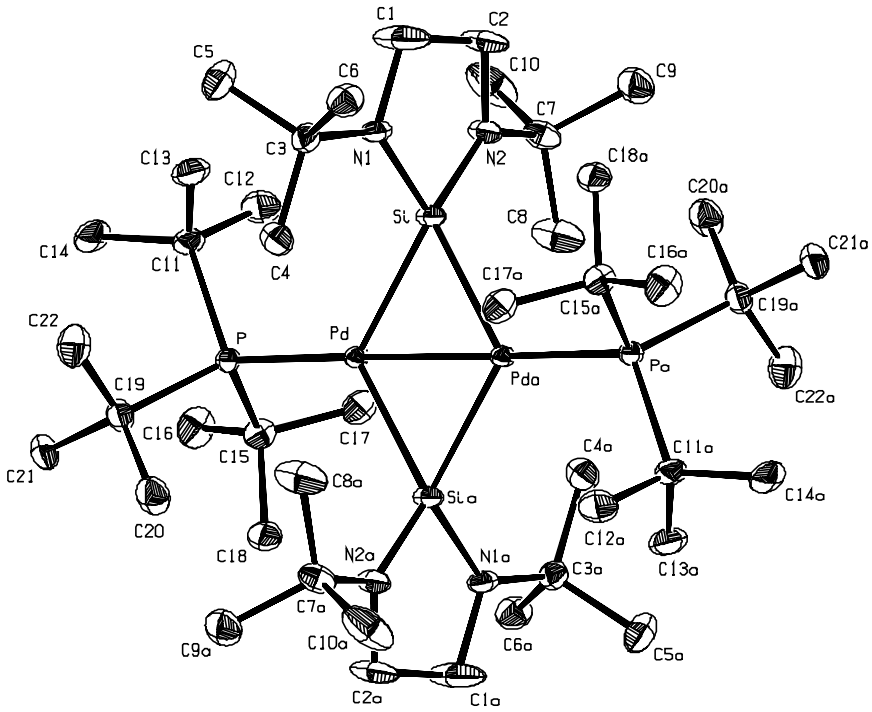


Fig. 4. ORTEP plot of complex **9** (without hydrogen atoms).

gassed. The NMR spectra were recorded in benzene-d_6 at room temperature (r.t.), using a Bruker DPX 400 at 400 MHz (^{1}H), 100.85 MHz (^{13}C), 116.98 MHz (^{31}P) and a JEOL JMX-GX at 79.4 MHz (^{29}Si). Bis(tri-*tert*-butylphosphine)palladium(0) [18] and dimethylpalladium(II)cyclooctadiene [19] as well as the free NHS **1** and **2** were prepared according to literature [8,9].

4.1. X-ray crystallography: data collection and refinement

Single crystals of the complexes **7** and **9** were grown from benzene at 25 °C. X-ray diffraction data were collected on a Nonius kappa-CCD-system [20]. Preliminary positions of heavy atoms were found by direct methods [21], while positions of the other non-hydrogen atoms were determined from successive Fourier difference maps coupled with initial isotropic least-square refinement [22]. All of the non-hydrogen positions were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined using a riding model. All details of the data collection, the crystal and refinement parameters are summarized in Table 2.

4.2. $[\overline{Si(^tBuNCH_2CH_2N^tBu)}]_4Pd$ (**6**)

In a glovebox, 7.3 mg (0.03 mmol) of $PdMe_2(COD)$ was dissolved in 0.3 ml benzene-d_6, and 35.5 mg (0.18 mmol) of Si(^{t}BuNCH$_2$CH$_2$N^{t}Bu) in 0.5 ml benzene-d_6 was added. After stirring for 24 h, the initially red solution turned pale yellow. The product **6** was characterized by NMR. Upon concentration, precipitation of palladium-black was observed.

^{1}H-NMR (ppm): δ 1.44 (N^{t}Bu, 72H, s), 3.19 (NCH$_2$, 16H, s); ^{13}C{^{1}H}-NMR (ppm): δ 32.2 (C*Me*$_3$), 45.8 (N*C*H$_2$), 52.7 (*C*Me$_3$).

4.3. $[\overline{Si(^tBuNCH_2CH_2N^tBu)}]_2[P(^tBu)_3]_2Pd_2$ (**7**)

Pd[P(^{t}Bu)$_3$]$_2$ (153.7 mg, 0.30 mmol) was dissolved in 10 ml benzene. A solution of Si(^{t}BuNCH$_2$CH$_2$N^{t}Bu) (125.3 mg, 0.63 mmol) in 10 ml benzene was added at r.t. Instantly, the solution turned deep red, and it was stirred for 30 min. Upon concentration in vacuum, **7** was obtained as red crystals suitable for X-ray structure determination after several days at r.t. (191 mg, 63%).

^{1}H-NMR (ppm): δ 1.50 (N^{t}Bu, 36H, s), 1.57 (P^{t}Bu, 18H, d), 3.23 (NCH$_2$, 8H, s); ^{13}C{^{1}H}-NMR (ppm): δ 33.1 (PC(*C*H$_3$)$_3$, m), 37.4 (P*C*(*C*H$_3$)$_3$, d, $^1J_{CP} = 28.2$ Hz), 46.9 (N*C*H$_2$), 53.4 (N*C*(CH$_3$)$_3$); ^{31}P{^{1}H}-NMR (ppm): δ 93.36. Anal. Found: C, 52.3; H, 9.72; N, 5.57. Calc. for $C_{44}H_{98}N_4P_2Pd_2Si_2$: C, 52.1; H, 9.67; N, 5.52%.

4.4. $[\overline{Si(^tBuNCH{=}CHN^tBu)}]_3Pd$ (**8**)

A freshly prepared solution of 150 mg (0.61 mmol) $Pd(COD)Me_2$ was transferred to a solution of 700 mg (3.57 mmol) Si(^{t}BuNCH=CHN^{t}Bu) in 30 ml benzene. Immediately, a clear orange–red solution was observed, which turned deep red at the end of the addition. After stirring for 30 min, the mixture was refluxed for 4 h and

Table 2
Crystal data and structure refinement parameters for compounds **7** and **9**

	7	**9**
Empirical formula	$C_{44}H_{98}N_4P_2Pd_2Si_2$	$C_{44}H_{94}N_4P_2Pd_2Si_2$
Formula weight	1014.17	101.19
Temperature (K)	123	293
λ(Mo–K$_\alpha$) (Å)	0.71073	0.71373
Crystal system	Triclinic	Trigonal
Space group	$P\bar{1}$	$R\bar{3}$
Unit cell dimensions		
a (Å)	10.3988(1)	33.4806(2)
b (Å)	12.3172(1)	33.4806(2)
c (Å)	12.3344(1)	14.9087(1)
α (°)	102.4299(4)	90
β (°)	114.6975(5)	90
γ (°)	108.4758(9)	120
V (Å^3)	1245.63(2)	14472.94(16)
Z	1	9
ρ_{calc} (g cm^{-3})	1.352	1.043
μ (mm^{-1})	0.867	0.672
F(000)	540	4824
Crystal size (mm)	$0.51\times0.16\times0.10$	$0.53\times0.51\times0.33$
Diffractometer	Nonius-κCCD	Nonius-κCCD
Scan type	ω- and ρ-scan	ω- and ρ-scan
θ Range (°)	2.04–26.37	2.04–26.37
No. of total/unique data [$I>2\sigma(I)$]	16 791/4910	37 219/6565
No. of observed data	4532	5508
No. of parameters	254	244
Final R_1 [a]	0.0199	0.0214
Final wR_2 [b]	0.0460	0.0617
Goodness-of-fit [c]	1.076	0.990
Difference Fourier (e Å^{-3})	0.44/−0.37	0.28/−0.28

[a] $\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$.
[b] $[\Sigma w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.
[c] $[\Sigma w(F_o^2-F_c^2)^2/(N_{ref}-N_{var})]^{1/2}$.

a light red solution was formed. All volatile substances were evaporated and then the dimethyldiamidosilan and unconsumed silylene **2** were removed under vacuum at 60 °C via sublimation, resulting in an orange microcrystalline product **8** (0.3 g; 71%).

^{1}H-NMR (ppm): δ 1.54 (C(CH$_3$)$_3$, 18H, s), 6.71 (CH, 2 H, s); ^{13}C-NMR (ppm): δ 33.5 (C*Me*$_3$), 54.1 (*C*Me$_3$), 118.6 (*C*H); ^{29}Si-NMR (ppm): δ 113.6. Anal. Found: C, 52.67; H, 9.04. Calc. for $C_{30}H_{60}N_6PdSi_3\cdot1/10COD$: C, 52.36; H, 8.74%.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 176718 and 176717 for compounds **7** and **9**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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