DOI: 10.1002/ejic.201200247



## Bridging Pseudohalides in Palladacycles as a Source of Different Assemblies

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Keywords: Self-assembly / Bridging ligands / Palladium / Metallacycles / Silanes

The reaction of  $[Pd\{CH_2SiPh_2(CH_2NC_5H_{10})-\kappa^2C,N\}(\mu-Cl)]_2$ (CH<sub>2</sub>NC<sub>5</sub>H<sub>10</sub> = piperidinomethyl) with KSCN led to the centrosymmetric dimer  $[Pd\{CH_2SiPh_2(CH_2NC_5H_{10})-\kappa^2C,N\}(\mu-SCN-\kappa^1S,\kappa^1N)]_2$ , which features side-on bridging thiocyanate ligands. However, the analogous reaction of the chloridobridged starting material with NaN<sub>3</sub> yielded the dimer  $[Pd\{CH_2SiPh_2(CH_2NC_5H_{10})-\kappa^2C,N\}(\mu-N_3-\kappa^1\kappa^1N)]_2$ , in which the azido ligands exhibit end-on coordination. This complex persists as a mixture of *cis* and *trans* isomers in solution. Lastly, the square tetrametallic complex  $[Pd\{CH_2SiPh_2(CH_2NC_5H_{10})-\kappa^2C,N\}(\mu-CN-\kappa^1C,\kappa^1N)]_4$  was obtained from the reaction between the parent chlorido-

#### Introduction

In coordination chemistry, pseudohalides are interesting polyatomic ligands due to their ability to induce a variety of structural motifs. They often act as bridging ligands giving rise to different structures that may be discrete moieties, such as dimers, trimers, or tetramers, infinite assemblies, such as monodimensional chains, either ladder or helicoid type, or even two- or three-dimensional cages. The final structure depends both on the electronic and structural requirements of both the pseudohalide and the metal fragment used. The donor atoms and the directionality of the frontier orbital determine the coordination mode of the pseudohalide.<sup>[1]</sup>

Following our studies on the reactivity of (piperidinomethyl)silylmethyl cyclopalladated complexes,<sup>[2]</sup> we decided to explore the behavior of this soft metallic center with two coordinating sites available in *cis* geometry towards pseudohalides such as cyanide, thiocyanate, or azide, which present several possible coordination modes and give rise to different assemblies, as described herein.

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- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201200247.

bridged complex and AgCN. In solution, this compound forms an equilibrium between the tetra- and trimetallic species. Thermodynamic data (equilibrium constants and free energies in CDCl<sub>3</sub> and C<sub>6</sub>D<sub>6</sub>, and enthalpy and entropy in CDCl<sub>3</sub>) were determined and show that the formation of the trimetallic isomer is thermodynamically disfavored [ $K_{\rm eq} = (1.93 \pm 0.07) \times 10^{-4} \, {\rm mol} \, {\rm L}^{-1}$  and  $\Delta G_{\rm eq} = 20.83 \pm 0.11 \, {\rm kJ} \, {\rm mol}^{-1}$  in CDCl<sub>3</sub>,  $K_{\rm eq} = (4.5 \pm 0.2) \times 10^{-5} \, {\rm mol} \, {\rm L}^{-1}$  and  $\Delta G_{\rm eq} = 24.40 \pm 0.14 \, {\rm kJ} \, {\rm mol}^{-1}$  in C<sub>6</sub>D<sub>6</sub>] and that the variation in the enthalpy and entropy are positive ( $\Delta H = 75 \pm 5 \, {\rm kJ} \, {\rm mol}^{-1}$  and  $\Delta S = 186 \pm 15 \, {\rm J} \, {\rm mol}^{-1} \, {\rm K}^{-1}$  in CDCl<sub>3</sub>).

The presence of a silicon atom in the (piperidinomethyl)silylmethyl cyclopalladated complexes is expected to play a dual role: stabilizing the metallated carbon atom by polarization effects and preventing  $\beta$ -elimination. The palladacycle is made possible by the presence of a nitrogen donor in the side-arm that can coordinate to the Pd<sup>II</sup> center, thereby forming the five-membered palladacycle. This chelating side-arm is an often employed tool, for example, in activating alkylsilanes towards metallation and in stabilizing the configuration of diastereomerically enriched  $\alpha$ -lithiated alkylsilanes in the case of chiral amine ligands.<sup>[3]</sup>

### **Results and Discussion**

Chlorido-bridged dimer  $[Pd{CH_2SiPh_2(CH_2NC_5H_{10})-\kappa^2C,N}(\mu-Cl)]_2$  (1) served as the starting material for the synthesis of new pseudohalido-bridged complexes. The pseudohalides employed were thiocyanate, azide, and cyanide and were introduced by the reaction of 1 with metal salts of the corresponding pseudohalide (Scheme 1).



Scheme 1. General synthesis of pseudohalide complexes by starting from 1.



The reaction of **1** with potassium thiocyanate in THF led to a new dimer,  $[Pd\{CH_2SiPh_2(CH_2NC_5H_{10})-\kappa^2C,N\}(\mu$ -SCN- $\kappa^1S,\kappa^1N)]_2$  (**2**) in which the pseudohalide acts as bridging ligand. In general, thiocyanate may coordinate in one of the three following modes: Side-on or end-on, and in the later case, with S or N as donor (cf. Figure 1). In this case, the IR spectrum of **2** immediately suggests a side-on coordination mode as its CN stretching absorption appears at 2137 cm<sup>-1</sup>, higher than would be expected for the two end-on coordination modes.<sup>[4]</sup>



Figure 1. Coordination modes for a bridging thiocyanato ligand.

The molecular structure of **2** obtained unambiguously supports this assignment (Figure 2). The compound crystallizes from hexane/dichloromethane with a tetragonal crystal system in the space group  $I4_1/a$ . The asymmetric unit contains one half of the centrosymmetric dimeric structure.



Figure 2. Molecular structure and numbering scheme of compound **2** in the crystal form (SCHAKAL plot).<sup>[12]</sup> Selected distances [Å] and angles [°]: C(1)–Pd 2.045(2), C(1)–Si 1.849(2), C(14)–Si 1.892(2), C(14)–N(1) 1.497(3), N(1)–Pd 2.1601(17), N(2)–Pd 2.1079(17), Pd–S 2.3071(6), S–C(20)<sup>#1</sup> 1.669(2), C(20)–N(2) 1.145(3); Si–C(1)–Pd 99.96(10), C(1)–Si–C(14) 104.05(10), N(1)–C(14)–Si 109.59(14), C(14)–N(1)–Pd 103.12(12), C(1)–Pd–N(2) 174.78(9), C(1)–Pd–N(1) 86.19(8), N(2)–Pd–N(1) 96.70(6), C(1)–Pd–S 83.49(7), N(2)–Pd–S 93.62(5), N(1)–Pd–S 169.67(5), N(2)–C(20)–S<sup>#1</sup> 179.7(2), C(20)–N(2)–Pd 160.31(16), C(20)<sup>#1</sup>–S–Pd 104.34(7). Symmetry operator: <sup>#1</sup>: -x + 1/2, -y + 3/2, -z + 1/2.

As the structure of **2** is a centrosymmetric dimer, the *trans* isomer is observed in which both carbon or both nitrogen donor atoms are at opposite sides of the molecule. The thiocyanate groups have a linear geometry [S–C–N 179.7(2)°] and the S–C and C–N distances are typical of double bonds.<sup>[5]</sup> The thiocyanato bridging ligands form an eight-membered, nearly planar ring with both palladium centers. The slight distortion from planarity is reflected in the dihedral angle N–Pd–S–C20 of 8.0(4)° between the metal atoms and the bridging ligands. This value is similar to those found in other palladium complexes with bridging thiocyanato ligands, such as 11.9(3)° for [P(CH<sub>2</sub>Ph)Ph<sub>3</sub>]<sub>2</sub>-[(C<sub>6</sub>F<sub>3</sub>H<sub>2</sub>)<sub>2</sub>Pd( $\mu$ -SCN)( $\mu$ -NCS)Pd(C<sub>6</sub>F<sub>3</sub>H<sub>2</sub>)<sub>2</sub>]<sup>[6]</sup> or 5.2(4)° for [Pd(*C*<sup>2</sup>,*N*-dmba)( $\mu$ -SCN)]<sub>2</sub>,<sup>[7]</sup> but slightly larger than

those found in palladacycles with metallated chiral ferrocenylimines<sup>[8]</sup> and benzylideneaniline.<sup>[9]</sup>

Each palladium atom is also coordinated by the nitrogen and carbon donor atoms of the  $[CH_2SiPh_2(CH_2NC_5H_{10})]$ moiety, thereby forming the palladacycle. The Pd–C distance of 2.045(2) Å is in the range typically found for Pd–  $C(sp^3)$  single bonds.<sup>[10]</sup>

The conformation of the five-membered silapalladacycle may be described as an envelope in which the average dihedral angle of the palladium center with respect to the other four atoms is  $36.2(2)^\circ$ . The presence of palladium and silicon in the five-membered palladacycle results in a short Pd···Si distance of 2.985(1) Å, and the Si–C1–Pd angle is  $100.0(1)^\circ$ . These distances and angles in the silapalladacycle are in the range of those previously found.<sup>[2]</sup>

The nitrogen atoms of the bridging thiocyanate and the cyclometallated ligand are coordinated in *cis* geometry. This is to be expected taking into account the higher *trans* influence of the carbon donor ligand and of the sulfur donor atom in the bridging thiocyanate compared with the lower *trans* influence of the two nitrogen donors. This is a result of the antisymbiotic effect of the palladium(II) soft metal center.<sup>[11]</sup>

In solution, only one isomer of **2** was detected (see the Exp. Sect.). This suggests that the above geometry is maintained in solution, because any of the end-on modes would give rise to *cis* and *trans* geometries. A singlet signal is observed for each methylene group of the palladacycle (PdCH<sub>2</sub>Si and SiCH<sub>2</sub>N), which results from the fast dynamic process usually observed in five-membered metallacycles with an envelope conformation in which the Si and C atoms move from one side of the plane to the other, making both sides equivalent.

A mixture of isomers was obtained in solution after reaction of the parent chlorido-bridging dimer 1 with sodium azide, which gave  $[Pd\{CH_2SiPh_2(CH_2NC_5H_{10})-\kappa^2C,N\}(\mu-N_3-\kappa^1\kappa^1N)]_2$  (3). Like the thiocyanate, the azido ligand may also coordinate side-on (Figure 3, **a**) or end-on (Figure 3, **b**). In contrast to thiocyanate, in this case IR spectroscopy does not allow differentiation between coordination modes as the N=N stretching absorptions are very similar. An endon coordination is proposed for 3, as occurs in the few reported examples of structures with bridging azides coordinated to palladium(II).<sup>[13]</sup> Single crystals obtained from 3 confirmed this connectivity; however, the overall quality of the data was insufficient to merit publication.<sup>[14]</sup>



Figure 3. Possible coordination modes for a bridging azido ligand.

Two signal sets are detected in the <sup>1</sup>H and <sup>13</sup>C NMR spectra of **3**, which suggests the presence of two isomers in solution. The most informative signals are those of the methylene groups PdCH<sub>2</sub>Si and SiCH<sub>2</sub>N, which resonate at  $\delta \approx 1$  and 3 ppm, respectively, in the <sup>1</sup>H NMR spectra and

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at  $\delta \approx 5$  and 50 ppm, respectively, in the <sup>13</sup>C NMR spectra. For **3**, the two isomers coexist in a ratio of 55:45 in CDCl<sub>3</sub>. When the spectrum was recorded in  $(CD_3)_2CO$ , the ratio changed to 60:40 (see the Exp. Sect.). This led to the assignment of the major isomer observed to *cis* and the minor isomer to *trans* on the basis of the higher polarity of the *cis* isomer and acetone relative to the *trans* form and chloroform. Thus, the two isomers clearly undergo a slow equilibrating process in solution (Scheme 2). However, the *trans* structure is exclusively observed in the crystal. This observation has also been made for the parent chlorido-bridged complex 1.<sup>[2b]</sup>



Scheme 2. Isomers of 3 detected in solution.

The third pseudohalide studied was cyanide. Whereas azide and thiocyanate coordinate as bridging ligands in dimetallic species with bent geometries, cyanide, given its tendency to form linear bridges, should promote a different mode of assembly. Thus, parent chlorido-bridged dimer **1** was treated with equimolar amounts of silver cyanide leading to the precipitation of AgCl and the formation of the tetrametallic complex  $[Pd{CH_2SiPh_2(CH_2NC_5H_{10})-\kappa^2C,N}(\mu-CN-\kappa^1C,\kappa^1N)]_4$  (**4**). The crystals obtained were subjected to crystal structure determination, which gave the structure shown in Figure 4.<sup>[13]</sup>

Complex 4-hexane crystallizes from dichloromethane/ hexane in the monoclinic crystal system. The asymmetric unit contains two independent molecules of the tetrametallacycle 4 and two disordered hexane molecules. Each molecule of 4 contains four palladium centers bridged by cyanido ligands. However, the structural determination does not allow differentiation of the carbon and nitrogen atoms of the bridging cyanide. Therefore, the structure was refined by taking into account the antisymbiotic effect of the soft palladium(II) center,<sup>[11]</sup> which led to the proposal of mutual cis coordination of both carbon donor ligands (i.e., methylene and cyanide-C, with higher trans influence) and both nitrogen donor ligands (i.e., piperidyl and cyanide-N, with lower *trans* influence). A cyclometalated (piperidinomethyl)silylmethyl moiety is also coordinated to each palladium center. The bridging cyanides are essentially linear: The Pd-C-N angles range from 175.5(7) to 179.5(8)°, and the C-N-Pd angles are in the range 167.3(6)-178.0(5)°. These angles and the C-N distances are similar to those found in other tetranuclear complexes with bridging cyanides.<sup>[15]</sup> The four palladium atoms are not coplanar, but form a dihedral angle of 27°. With dihedral angles found in similar tetrametallic structures ranging from 0 to 35°, this deviation from planarity is relatively distinct.



Figure 4. Molecular structure and numbering scheme of compound 4 in the crystal (only one of the two independent molecules in the asymmetric unit is shown, SCHAKAL plot).<sup>[12]</sup> Peripheral hydrogen atoms outside the palladacycles have been omitted for clarity. Selected distances [Å] and angles [°]: Pd1-Si1 3.088(2), Pd1-N1 2.178(5), Pd1-N2 2.089(6), Pd1-C1 2.064(8), Pd1-C80 1.928(6), Pd2-Si2 3.051(2), Pd2-N3 2.185(7), Pd2-N4 2.096(5), Pd2-C20 1.9154(7), Pd2-C21 2.0608(6), Pd3-N5 2.1977(5) Pd3-N6 2.0992(6), Pd3-C40 1.936(6), Pd3-C41 2.055(7), Pd4-Si4 3.030(2), Pd4-N7 2.180(6), Pd4-N8 2.093(5), Pd4-C60 1.943(7), Pd4-C61 2.058(6), N2-C20 1.188(10), N4-C40 1.168(8), N6-C60 1.160(9), N8-C80 1.174(8); Pd1-N2-C20 178.2(6), Pd2-N4-C40 170.2(5), Pd3-N6-C60 175.8(6), Pd4-N8-C80 171.1(6), Pd1-C1-Si1 103.6(4), Pd2-C21-Si2 102.4(3), Pd3-C41-Si3 105.4(4), Pd4-C61-Si4 101.2(3), Pd1-N2-C20 178.2(6), Pd2-N4-C40 170.2(5), Pd3-N6-C60 175.8(6), Pd4-N8-C80 171.1(6), Pd2-C20-N2 178.4(6), Pd3-C40-N4 179.4(6), Pd4-C60-N6 178.0(6), Pd1-C80-N8 178.3(6).

The Pd–C distances [2.028(7)–2.061(6) Å] are in the range found for Pd–C(sp<sup>3</sup>) single bonds.<sup>[10]</sup> The conformation of the five-membered palladacycles may be described as envelopes: The dihedral angles of the palladium atoms with respect to the other four atoms range from 31.6° for Pd(3) to 36.2° for Pd(1), as is usually found in these metallacycles. As with compounds 1 and 2, the distance between the palladacycles in 4 is short; however, the Pd···Si distances in the tetrametallacycle are slightly longer than those observed in the thiocyanato-bridged dimer 2 and range from 3.015(2) to 3.117(2) Å. These distances and angles in the silapalladacycles are similar to those previously found.<sup>[2]</sup>

The structure found in the solid is not maintained in solution, as evidenced by the NMR spectra displaying signals from two different species. The signals of the methylene groups NCH<sub>2</sub>Si and SiCH<sub>2</sub>Pd allowed a quantitative analysis of the concentration of each isomer. The two species

are present in a ratio that depends on the concentration, temperature, and solvent, but one of the isomers is always dominant. To assign unequivocally the signals to each isomer, an NMR sample of 4 in frozen CDCl<sub>3</sub> was prepared in a liquid-nitrogen bath and then allowed to melt and simultaneously dissolve at -40 °C in the NMR probe. The <sup>1</sup>H NMR spectrum immediately recorded under these conditions showed only signals from the major isomer, which led to the conclusion that the major isomer in solution is always the tetranuclear complex detected in the crystal structure. The concentration of the minor isomer is higher in diluted solutions and at higher temperatures, and in polar CDCl<sub>3</sub> compared with nonpolar C<sub>6</sub>D<sub>6</sub>. On the other hand, the IR spectra only show one CN stretching absorption in the solid state (2162 cm<sup>-1</sup>) as well as in CH<sub>2</sub>Cl<sub>2</sub> (2159 cm<sup>-1</sup>) and toluene (2164 cm<sup>-1</sup>) solutions. As IR spectroscopy is a fast technique on the spectroscopic timescale, that is, it differentiates between species present in solution even when they are involved in slow processes in solution, the conclusion is that the CN stretching absorption is the same for both isomers.

All these data are in accord with the equilibrium proposed in Scheme 3 between the tetrametallic complex detected in the crystal structure and a trimetallic species. This type of equilibria has been found for other tetrametallic complexes, and the factors controlling the tetrametallic/trimetallic equilibria have recently been the target of extensive studies.<sup>[16]</sup>

In our case, the ratio of tetrametallic/trimetallic species in CDCl<sub>3</sub> increases with concentration, with values of 80:20 at 0.08 mequiv. mL<sup>-1</sup> and 69:31 at 0.003 mequiv. mL<sup>-1</sup> (see Table 1), which leads to an equilibrium constant,  $K_{eq}$ , of  $(1.93 \pm 0.07) \times 10^{-4} \text{ mol L}^{-1}$  and a free energy,  $\Delta G_{eq}$ , of  $20.83 \pm 0.11 \text{ kJ mol}^{-1}$  (see the Supporting Information) for the equilibrium depicted in Scheme 3.

A study of the concentrations of the isomers as a function of temperature allowed us to determine the values of  $\Delta H_{\rm eq}$  and  $\Delta S_{\rm eq}$  for the equilibrium process (Table 2) from the van't Hoff equation (1).

$$\ln K_{\rm eq} = -(\Delta G_{\rm eq}/RT) = -(\Delta H_{\rm eq}/RT) + (\Delta S_{\rm eq}/R)$$
(1)



Table 1. Thermodynamic data for the equilibrium detected in solutions of  $\mathbf{4}$  as a function of concentration.

Concentration [meq mL <sup>-1</sup> ]	Trimetallic [%]	Tetrametallic [%]
0.080	20	80
0.050	22	78
0.025	25	75
0.012	28	72
0.006	30	70
0.003	31	69

Table 2. Thermodynamic data for the equilibrium detected in the solutions of **4** as a function of temperature.

T [K]	Trimetallic [%]	Tetrametallic [%]	K <sub>eq</sub>
253	6	94	$9.86 \times 10^{-7}$
273	13	87	$2.74 \times 610^{-5}$
293	20	80	$1.98 \times 10^{-4}$
313	30	70	$1.49 \times 10^{-3}$

As expected, the enthalpy of the process depicted in Scheme 3 is positive ( $\Delta H = 75 \pm 5 \text{ kJ mol}^{-1}$ ), which reflects the lower strain of the tetrametallic structure, and the entropy is quite large and also positive ( $186 \pm 15 \text{ J mol}^{-1} \text{ K}^{-1}$ ), which reflects the higher disorder that results from the greater number of particles when trimetallic isomers are formed from tetrametallic isomers.

These thermodynamic values are similar to those obtained for similar equilibria previously reported between tetra- and trimetallic palladium complexes.<sup>[16d-16f]</sup> An important difference between complex **4** and those previously described is that **4** is neutral, whereas those reported in the literature are cationic. This might be the cause of their different behavior when the polarity of the solvent changes: for the cationic complexes, the equilibrium is shifted towards the trimetallic isomer as the solvent polarity increases,<sup>[16d,16f]</sup> whereas for **4**, the equilibrium constant detected in nonpolar C<sub>6</sub>D<sub>6</sub> is smaller [ $K_{eq} =$  $(4.5 \pm 0.2) \times 10^{-5} \text{ mol L}^{-1}$ ], and thus the free energy is higher ( $\Delta G_{eq} = 24.40 \pm 0.14 \text{ kJ mol}^{-1}$ ; see the Supporting Information) than in CDCl<sub>3</sub> (see above). This feature might be interpreted on the basis that the equilibrium proposed in Scheme 2 should occur through a dissociative mechanism



Scheme 3. Isomers detected in solutions of 4.

due to metal-ligand bond cleavage, and therefore polar solvents should favor this step.

## Conclusions

The coordination of the pseudohalides cyanide, thiocyanate, or azide to a "soft"  $Pd^{II}$  center with two potential coordinating positions in *cis* geometry led to different types of assemblies. The bridging azide and thiocyanate give rise to dimetallic species in which the azide is coordinated endon and the thiocyanate is coordinated side-on. In contrast, the linear bridging cyanide gives rise to a square-shaped tetrametallic complex. The latter is in equilibrium with a trimetallic isomer in solution, whereas the bridging azide dimer persists as a mixture of *cis* and *trans* isomers in solution. The trimetallic species is always the minor isomer, but its ratio increases with dilution, increasing temperature, and increasing polarity of the solvent used.

## **Experimental Section**

**General:** IR (KBr pellets, 4000–450 cm<sup>-1</sup>): Perkin–Elmer Spectrum RX I FT-IR spectrometer. <sup>1</sup>H NMR [solvent CDCl<sub>3</sub>; internal standard: CHCl<sub>3</sub> ( $\delta$  = 7.24 ppm); recorded at room temperature]: Bruker AC-300 or ARX-300 spectrometer (300.13 MHz). <sup>13</sup>C NMR [solvent and internal standard: CDCl<sub>3</sub> ( $\delta$  = 77.00 ppm); recorded at room temperature; integrations are indicated per "CH<sub>2</sub>SiPh<sub>2</sub>(CH<sub>2</sub>NC<sub>5</sub>H<sub>10</sub>)" unit]: Bruker ARX-300 spectrometer (75.78 MHz). Assignment of the <sup>13</sup>C NMR spectroscopic data is supported by DEPT experiments and the relative intensities of the resonance signals. Microanalyses: Perkin-Elmer 2400B microanalyzer, Área de Química Inorgánica, Facultad de Ciencias, Valladolid (Spain). All reactions were carried out under oxygen-free and dried dinitrogen according to conventional Schlenk techniques. The solvents were dried according to common procedures. Complex 1 was obtained as described previously.[2b] The other reactants were obtained from the usual commercial suppliers.

 $[Pd{CH_2SiPh_2(CH_2NC_5H_{10})-\kappa^2C,N}(\mu-SCN-\kappa^1S,\kappa^1N)]_2$  (2): A mixture of 1 (0.087 g, 0.1 mmol) and KSCN (0.097 g, 1.0 mmol) in THF (10 mL) was stirred at 40 °C for 15 h. The volatiles were removed in vacuo, and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (ca. 20 mL). The yellow solution was filtered, and hexane (ca. 10 mL) was added. Concentration in vacuo and cooling to -20 °C afforded yellow crystals, which were decanted, washed with hexane (3  $\times$ 3 mL), and vacuum-dried to yield 0.052 g (57%) of 2. IR (KBr):  $\tilde{v}$ = 3066 (m), 2945 (s), 2856 (s), 2808 (m), 2137 (vs), 1587 (w), 1567 (w), 1486 (w), 1468 (m), 1442 (s), 1426 (m), 1374 (w), 1298 (w), 1282 (w), 1261 (w), 1225 (w), 1175 (w), 1111 (s), 1039 (m), 998 (m), 910 (w), 882 (w), 862 (m), 797 (m), 765 (s), 720 (s), 698 (s), 575 (w), 551 (m), 508 (s), 491 (s), 461 (m), 419 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$ = 7.65 (m, 4 H,  $C_6H_5$ ), 7.38 (m, 6 H,  $C_6H_5$ ), 3.34 (m, 2 H,  $CH_2$ pip), 2.98 (s, 2 H, NCH<sub>2</sub>Si), 2.36 (m, 2 H, CH<sub>2</sub> pip), 1.86 (m, 2 H, CH<sub>2</sub> pip), 1.66 (m, 3 H, CH<sub>2</sub> pip), 1.37 (m, 1 H, CH<sub>2</sub> pip), 0.64 (s, 2 H, SiCH<sub>2</sub>Pd) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  = 136.5 (s, SiC<sub>6</sub>H<sub>5</sub> *ipso*), 134.7 (s, SiC<sub>6</sub>H<sub>5</sub> ortho), 129.3 (SiC<sub>6</sub>H<sub>5</sub> para), 127.9 (SiC<sub>6</sub>H<sub>5</sub> meta), 126.7 (s, SCN), 62.7 (s, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 55.0 (s, NCH<sub>2</sub>Si), 23.1 (s, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 22.9 (s, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.3 (s, PdCH<sub>2</sub>Si) ppm. C<sub>40</sub>H<sub>48</sub>N<sub>4</sub>Pd<sub>2</sub>S<sub>2</sub>Si<sub>2</sub> (917.94): calcd. C 52.34, H 5.27, N 6.10; found C 52.11, H 5.14, N 5.96.

 $[Pd{CH_2SiPh_2(CH_2NC_5H_{10})-\kappa^2C,N}(\mu-N_3-\kappa^1\kappa^1N)]_2$  (3): A mixture of 1 (0.087 g, 0.1 mmol) and NaN<sub>3</sub> (0.014 g, 0.22 mmol) in THF (10 mL) was stirred at 40 °C for 15 h. The volatiles were removed in vacuo, and the residue was extracted with toluene (ca. 20 mL). The yellow solution was filtered and concentrated in vacuo, and hexane (ca. 10 mL) was added. Cooling to -20 °C afforded yellow crystals, which were decanted, washed with hexane  $(3 \times 3 \text{ mL})$ , and vacuum-dried to yield 0.040 g (46%) of 3. IR (KBr):  $\tilde{v} = 3064$  (w), 2943 (w), 2860 (w), 2050 (vs), 1448 (w), 142 7 (m), 1357 (w), 1285 (m), 1261 (w), 1234 (w), 1110 (s), 1029 (m), 998 (m), 947 (w), 867 (m), 804 (s), 733 (s), 699 (s), 622 (w), 550 (m), 504 (w), 489 (m), 466 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  = 7.73 (m, 4 H, C<sub>6</sub>H<sub>5</sub>, 2 isomers), 7.40 (m, 6 H, C<sub>6</sub>H<sub>5</sub>, 2 isomers), 3.17 (m, 2 H, CH<sub>2</sub> pip, 2 isomers), 3.08 (s, 2 H, NCH<sub>2</sub>Si, 2 isomers), 2.50 (m, 2 H, CH<sub>2</sub> pip, 2 isomers), 1.77 (m, 5 H, CH<sub>2</sub> pip, 2 isomers), 1.44 (m, 1 H, CH<sub>2</sub> pip, 2 isomers), 1.25 (s, 2 H, SiCH<sub>2</sub>Pd, cis isomer), 1.12 (s, 2 H, SiCH<sub>2</sub>Pd pip, *trans* isomer) ppm; ratio *cis/trans* = 55:45. <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  = 136.3 (s, SiC<sub>6</sub>H<sub>5</sub> ipso, cis isomer), 136.2 (s, SiC<sub>6</sub>H<sub>5</sub> ipso, trans isomer), 134.6 (s,  $SiC_6H_5$  ortho, cis isomer), 134.5 (s,  $SiC_6H_5$  ortho, trans isomer), 129.4 (Si $C_6$ H<sub>5</sub> para, 2 isomers), 128.0 (Si $C_6$ H<sub>5</sub> meta, trans isomer), 127.9 (Si $C_6H_5$  meta, cis isomer), 61.6 (s, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, cis isomer), 61.4 (s, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, trans isomer), 55.5 (s, NCH<sub>2</sub>Si, cis isomer), 55.1 (s, NCH<sub>2</sub>Si, trans isomer), 22.9 (s, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, 2 isomers), 21.8 (s, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, cis isomer), 21.4 (s, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, trans isomer), 6.7 (s, PdCH<sub>2</sub>Si, cis isomer), 5.6 (s, PdCH<sub>2</sub>Si, *trans* isomer) ppm. C<sub>38</sub>H<sub>48</sub>N<sub>8</sub>Pd<sub>2</sub>Si<sub>2</sub> (885.82): calcd. C 51.62, H 5.46, N 12.55; found C 51.90, H 5.37, N 12.20.

 $[Pd{CH_2SiPh_2(CH_2NC_5H_{10})-\kappa^2C,N}(\mu-CN-\kappa^1C,\kappa^1N)]_4$  (4): A mixture of 1 (0.044 g, 0.05 mmol) and freshly prepared AgCN (from 0.019 g, 0.11 mmol of AgNO<sub>3</sub> and 0.007 g, 0.012 mmol of NaCN) in THF (5 mL) was stirred at room temp. for 3 h. Workup as for 3 gave 0.030 g (70%) of 4 as colorless crystals. IR (KBr):  $\tilde{v} = 3065$ (w), 3046 (m), 2938 (s), 2856 (m), 2813 (w), 2162 (s), 1451 (m), 1427 (s), 1381 (w), 1261 (w), 1109 (s), 1037 (m), 999 (w), 865 (w), 802 (m), 768 (s), 735 (s), 700 (vs), 557 (w), 503 (m), 488 (m), 473 (w), 437 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  = 7.66 (m, 4 H, C<sub>6</sub>H<sub>5</sub>, 2 isomers), 7.34 (m, 6 H, C<sub>6</sub>H<sub>5</sub>, 2 isomers), 3.25 (m, 2 H, CH<sub>2</sub> pip, 2 isomers), 2.75 (s, 2 H, NCH<sub>2</sub>Si, minor isomer), 2.73 (s, 2 H, NCH<sub>2</sub>Si, major isomer), 2.05 (m, 2 H, CH<sub>2</sub> pip, 2 isomers), 1.65 (m, 2 H, CH<sub>2</sub> pip, 2 isomers), 1.34 (m, 3 H, CH<sub>2</sub> pip, 2 isomers), 1.05 (m, 1 H, CH<sub>2</sub> pip, 2 isomers), 0.76 (s, 2 H, SiCH<sub>2</sub>Pd, minor isomer), 0.65 (s, 2 H,  $SiCH_2Pd$ , major isomer) ppm; ratio major/minor isomers = 80:20. <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  = 137.6 (s, SiC<sub>6</sub>H<sub>5</sub> *ipso*, minor isomer), 137.4 (s,  $SiC_6H_5$  ipso, major isomer), 134.9 (s,  $SiC_6H_5$  ortho, major isomer), 134.7 (s,  $SiC_6H_5$  ortho, minor isomer), 130.5 (s, CN, 2 isomers), 128.9 (SiC<sub>6</sub>H<sub>5</sub> para, 2 isomers), 127.6 (SiC<sub>6</sub>H<sub>5</sub> meta, 2 isomers), 61.5 (s, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, minor isomer), 60.7 (s, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, major isomer), 54.7 (s, NCH<sub>2</sub>Si, minor isomer), 53.2 (s, NCH<sub>2</sub>Si, major isomer), 23.1 (s, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, 2 isomers), 22.6 (s, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, 2 isomers), -7.6 (s, PdCH<sub>2</sub>Si, 2 isomers) ppm. C80H96N8Pd4Si4 (1707.64): calcd. C 51.62, H 5.46, N 12.55; found C 51.90, H 5.37, N 12.20.

X-ray Diffraction Study of 2 and 4: Crystals were grown by slow diffusion of hexane into concentrated solutions of the complexes in CH<sub>2</sub>Cl<sub>2</sub> at -20 °C. The crystallographic data were collected with a Stoe IPDS diffractometer and are presented in Table 3. The structures were solved by using direct and Fourier methods: Refinement by full-matrix least-squares methods (based on  $F_0^2$ ), anisotropic thermal parameters for all non-H atoms in the final cycles, H atoms were refined by using a riding model in their ideal geometric positions. SHELXS-86 and SHELXL-97 were used in the structural solutions and refinements.<sup>[17]</sup> CCDC-870641 (for 2) and -870642 (for 4) contain the detailed crystallographic data for this paper.

This data may be obtained free of charge from the Cambridge Crystallographic Data Center through www.ccdc.cam.ac.uk/data\_request/cif.

Table 3. Crystal and experimental data for compounds 2 and 4.

	2	4-hexane
Empirical formula	C40H48N4Pd2S2Si2	C <sub>86</sub> H <sub>110</sub> N <sub>8</sub> Pd <sub>4</sub> Si <sub>4</sub>
M [gmol <sup>-1</sup> ]	917.92	1793.78
Crystal system	tetragonal	monoclinic
Space group	$I4_1/a$	$P\overline{1}$
Crystal size [mm]	$0.20 \times 0.20 \times 0.20$	$0.20 \times 0.20 \times 0.10$
a [Å]	20.3965(9)	15.291(4)
<i>b</i> [Å]	20.3965(9)	23.438(5)
c [Å]	19.4889(13)	25.862(6)
a [°]	90	73.91(3)
β [°]	90	86.30(4)
γ [°]	90	73.32(3)
V [Å <sup>3</sup> ]	8107.7(7)	8530(3)
Ζ	8	4
$\rho_{\rm calcd.}  [\rm g  cm^{-3}]$	1.504	1.397
$\mu \text{ [mm^{-1}]}$	1.083	0.933
Refl. measured	44752	57780
Scan range [°]	$1.45 < 2\theta < 27.00$	$0.941 < 2\theta < 25.00$
Unique refl.	4420	28281
Refl. observed $[I > 2\sigma(I)]$	3777	17531
<i>R</i> 1, <i>wR</i> 2	0.0261, 0.0640	0.0576, 0.1499

**Supporting Information** (see footnote on the first page of this article): Thermodynamic data for the tetrametallic/trimetallic equilibrium of the CN-bridging complex in CDCl<sub>3</sub>, and ORTEP plot for molecular structure of **4**.

### Acknowledgments

The authors in Valladolid thank the Spanish Ministerio de Educación y Ciencia (CTQ2009-12111) and the Junta de Castilla y León (GR125 Programa de Grupos de Excelencia de la Junta de Castilla y León) for financial support. M. A. and P. G.-I. thank the Ministerio de Educación y Ciencia (MEC) and the Universidad de Valladolid (FPI Programs), respectively, for their grants. The authors in Dortmund thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and Wacker Chemie AG for their support.

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Received: March 10, 2012 Published Online: June 1, 2012