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[(Piperidinomethyl)silylmethyl] Cyclopalladated Complexes: Their Synthesis, Reactivity, and Solid State Structures[⊥]

Daniel Schildbach,[†] Marta Arroyo,[‡] Klaus Lehmen,[†] Susana Martín-Barrios,[‡] Luisa Sierra,[‡] Fernando Villafañe,*[,‡] and Carsten Strohmann*[,†]

Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany, and Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain

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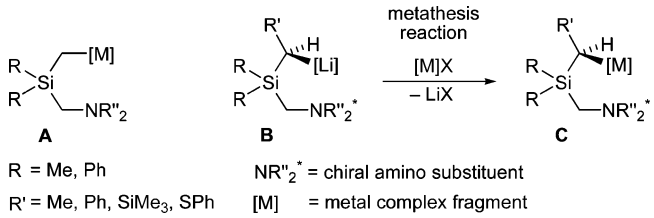
The reaction of $Ph_2Si(CH_2Li)(CH_2NC_5H_{10})$ (**2**) ($CH_2NC_5H_{10}$ = piperidinomethyl) with *trans*-$[PdCl_2(SMe_2)_2]$ leads to dimeric $[Pd\{CH_2SiPh_2(CH_2NC_5H_{10})\text{-}\kappa^2C,N\}(\mu\text{-}Cl)]_2$ (**3**), where the $[CH_2SiPh_2(CH_2NC_5H_{10})\text{-}\kappa^2C,N]$ ligand forms a palladacycle, as revealed by the crystal structure of the *transoid* isomer. In solution, this chloro-bridged dimer exists as a mixture of the *cisoid* and the *transoid* isomer. Monodentate ligands cleave the chloro bridges of dimer **3** to give compounds of the type $[Pd\{CH_2SiPh_2(CH_2NC_5H_{10})\text{-}\kappa^2C,N\}ClL]$ [L = PPh_3 (**4**), PMe_3 (**5**), CN^tBu (**6**), 4-methylpyridine (4-MePy) (**7**), tetrahydrothiophene (tht) (**8**), SMe_2 (**9**)], where the incoming ligand and the metalated carbon center are coordinated *cis*. The tetrafluoroborate salt of the cationic complex $[Pd\{CH_2SiPh_2(CH_2NC_5H_{10})\text{-}\kappa^2C,N\}(4\text{-MePy})_2]$ (**11**) is obtained by treating the starting dimer **3** with $TlBF_4$ and 4-MePy. The addition of $Ph_2PCH_2CH_2PPh_2$ (dppe) to the starting dimer **3** leads to $[\{Pd_2[CH_2SiPh_2(CH_2NC_5H_{10})\text{-}\kappa^2C,N]_2Cl_2\}(\mu\text{-dppe})]$ (**13**) or to $[Pd\{CH_2SiPh_2(CH_2NC_5H_{10})\text{-}\kappa^2C,N\}(dppe)]Cl$ (**11**), depending on the stoichiometry. NMR data reveal that the Pd−N bond in **11** is transiently opened in solution. $[Pd\{CH_2SiPh_2(CH_2NC_5H_{10})\text{-}\kappa^2C,N\}(dppe)]BF_4$ (**14**) is obtained from the latter compound upon treatment with $TlBF_4$. The chelate complexes $[Pd\{CH_2SiPh_2(CH_2NC_5H_{10})\text{-}\kappa^2C,N\}(acac)]$ (**16**) (acac = acetylacetonate) and $[Pd\{CH_2SiPh_2(CH_2NC_5H_{10})\text{-}\kappa^2C,N\}(S_2CNEt_2)]$ (**15**) are obtained by reaction of the starting chloro-bridged dimer **3** with Tl(acac) and NaS_2CNEt_2, respectively. The solid state structures of palladacycles **3**, **4**, **8**, **9**, **10**, and **15** were determined by X-ray diffraction methods.

Introduction

As part of our systematic studies on metalated organosilanes, we are interested in the structure and reactivity of [(aminomethyl)silylmethyl]metal compounds (type **A**).[1,2a,b] Two stabilizing effects play a role in these metal alkyls: the silicon center prevents β-hydrogen elimination and stabilizes the metalated α-carbon center. The (aminomethyl) substituent coordinates to the reactive center (intramolecular stabilization by chelation) and can induce the essential stereochemical information when chiral amines are introduced. Thus, this concept allowed the synthesis of highly diastereomerically enriched [(aminomethyl)silylmethyl]-lithium compounds—where the metalated carbon center is a stereogenic center with a defined absolute configuration (type **B**)[2]—leading to two areas for further study: (a) determining and understanding the directing factors for the regioselective and/or stereoselective metalation of organosilanes and (b) transferring the stereogenic lithiated carbon centers to organic molecules, heteroelement systems, or different metal complex fragments by metathesis reactions (type **C**) (Scheme 1).

Scheme 1



Herein we report on the coordination of an [(aminomethyl)silylmethyl] ligand, in particular [(piperidinomethyl)silylmethyl] ($[CH_2SiPh_2(CH_2NC_5H_{10})\text{-}\kappa^2C,N]$), to

[⊥] Dedicated to Professor Wolfdieter A. Schenk on the occasion of his 60th birthday.

* Corresponding authors. E-mail (C.S.): mail@carsten-strohmann.de; (F.V.) fervilla@qi.uva.es.

[†] Universität Würzburg.

[‡] Universidad de Valladolid.

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palladium complex fragments. There are very few reports on palladium complex fragments with [(aminomethyl)silylmethyl] ligands, which has prompted us to investigate the chemical behavior of the nonchiral ligand [$CH_2SiPh_2(CH_2NC_5H_{10})$-$\kappa^2C,N$] prior to any attempt to coordinate a chiral ligand. The rarity of palladium complexes with these types of nonchiral ligands makes the corresponding cyclopalladated complexes systems of great synthetic interest, especially in order to approach the corresponding enantiomerically enriched systems of type **C**.

Cyclopalladated complexes are important in several areas, from the synthesis of organic compounds to interdisciplinary aspects, such as their use in the design of new materials.[3] The system more commonly used is a five-membered orthometalated ring containing an sp^2-hybridized carbon and the nitrogen center of an amine as donor atoms,[4] although palladacycles of rather complicated structures may be designed and have been described.[4] However, this variety has not been extended to the presence of heteroatoms in the palladacycle in order to elucidate how these heteroatoms would affect the stability, the chemical properties, and the structural aspects of compounds of this type. There are only very few precedents of palladacycles containing silicon centers in the ring.[5]

Results and Discussion

Synthesis of [Pd{$CH_2SiPh_2(CH_2NC_5H_{10})$-$\kappa^2C,N$}-($\mu$-Cl)]$_2$ (3). The reaction between equimolar amounts of the organolithium compound $Ph_2Si(CH_2Li)(CH_2NC_5H_{10})$ (**2**)[1e] and *trans*-$[PdCl_2(SMe_2)_2]$ leads to the dimer [Pd{$CH_2SiPh_2(CH_2NC_5H_{10})$-$\kappa^2C,N$}($\mu$-Cl)]$_2$ (**3**) in 72% yield (Scheme 2). The doubly cyclometalated mononuclear complex [Pd{$CH_2SiPh_2(CH_2NC_5H_{10})$-$\kappa^2C,N$}$_2$] could not be detected. This is in contrast to the observation that complexes of the type $[PdCl_2(SR_2)_2]$ tend to give symmetrical doubly cyclometalated compounds when treated with the appropriate organolithium reagents.[6]

The attempts to coordinate the [(aminomethyl)silylmethyl] ligand by direct metalation of the aliphatic carbon by treating $Ph_2SiMe(CH_2NC_5H_{10})$ (**1**) with palladium acetate were not successful: deposition of metallic palladium was observed, and only unreacted silane was recovered from the solution. This method had been successively employed to coordinate 2-(trimethylsilyl)-pyridine or α-(trimethylsilyl)-8-methylquinoline to palladium(II),[5a,7] although these complexes were not crystallographically characterized. Furthermore, there are only a few reports on solid state structural determinations of silapalladacycles[5b,c] and of (silylmethyl)palladium compounds.[6,8]

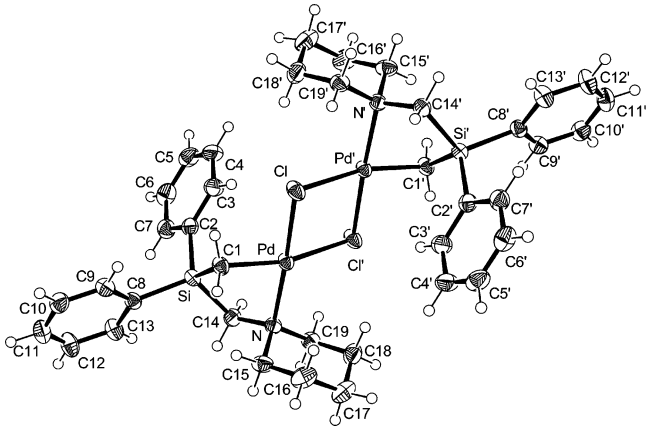


Figure 1. Molecular structure and numbering scheme of compound **3** in the crystal (ORTEP plot, ellipsoids drawn at 50% probability level). Selected distances (Å) and angles (deg): Pd−C(1) 2.034(2), Pd−N 2.126(2), Pd−Cl 2.329(1), Pd−Cl′ 2.491(1), Pd−Si 2.915(1), Si−C(1) 1.855(3), C(1)−Pd−N 86.81(9), C(1)−Pd−Cl 89.21(7), N−Pd−Cl 175.72-(6), C(1)−Pd−Cl′ 163.51(8), Pd−Cl−Pd′ 95.26(3), Cl−Pd−Cl′ 84.74(3), C(1)−Si−C(14) 104.4(1), Si−C(1)−Pd 97.0(1), C(14)−Si−Pd 70.43(7), N−C(14)−Si 108.2(2).

The molecular structure found for **3** and relevant distances and angles are shown in Figure 1. The geometry observed is the *transoid* isomer of the dimer, which is centrosymmetrical, the palladium and chlorine centers of the central four-membered ring being coplanar. This is in sharp contrast to the reported structure of the complex [Pd{$C(SiMe_3)_2SiMe_2(2\text{-}C_5H_4N)$-$\kappa^2C,N$}($\mu$-Cl)]$_2$ (2-C_5H_4N = 2-pyridinyl),[5b] where the dihedral angle between the coordination planes at the Cl−Cl axis is 60°. In this case, the cyclometalated ligand is bulkier and has more donor potential (two $SiMe_3$ substituents instead of two hydrogen atoms). At the same time, it is more π-acidic (pyridine instead of piperidine) than our [(piperidinomethyl)silylmethyl] ligand. It has been suggested that bent halogen-bridged complexes are formed when the ligands are strong σ-donors and/or strong π-acceptors.[9] Each palladium

(3) For examples see: (a) Ryabov, A. D. *Synthesis* **1985**, 233. (b) Newkome, G. R.; Puckett, W. E.; Gupta, V. K.; Kiefer, G. E. *Chem. Rev.* **1986**, *86*, 451. (c) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403. (d) Pfeffer, M. *Pure Appl. Chem.* **1992**, *64*, 335. (e) Wild, S. B. *Coord. Chem. Rev.* **1997**, *166*, 291. (f) Steenwinkel, P.; Gossage, R. A.; van Koten, G. *Chem. Eur. J.* **1998**, *4*, 759. (g) Herrmann, W. A.; Böhm, V. P. W.; Reisinger, C.-P. *J. Organomet. Chem.* **1999**, *576*, 23. (h) Rybtschinski, B.; Milstein, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 870. (i) Espinet, P.; Esteruelas, M. A.; Oro, L. A.; Serrano, J. L.; Sola, E. *Coord. Chem. Rev.* **1992**, *117*, 215. (j) Navarro-Ranninger, C.; López-Solera, I.; González, V. M.; Pérez, J. M.; Álvarez-Valdés, A.; Martín, A.; Raithby, P.; Masaguer, J. R.; Alonso, C. *Inorg. Chem.* **1996**, *35*, 5181. (k) Gianini, M.; von Zelewsky, A.; Stoeckli-Evans, H. *Inorg. Chem.* **1997**, *36*, 6094. (l) Albert, J.; Cadena, J. M.; Granell, J.; Muller, G.; Ordinas, J. I.; Panyella, D.; Puerta, C.; Sañudo, C.; Valerga, P. *Organometallics* **1999**, *18*, 3511. (m) He, G.; Mok, K. F.; Leung, P.-H. *Organometallics* **1999**, *18*, 4027. (n) Vicente, J.; Saura-Llamas, I.; Turpín, J.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **1999**, *18*, 2683. (o) Zhao, G.; Yang, Q.-C.; Mak, T. C. W. *Organometallics* **1999**, *18*, 3623. (p) Dupont, J.; Pfeffer, M.; Spencer, J. *Eur. J. Inorg. Chem.* **2001**, 1917.

(4) Canty, A. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford (UK), 1995; Vol. 9, Chapter 5.5.

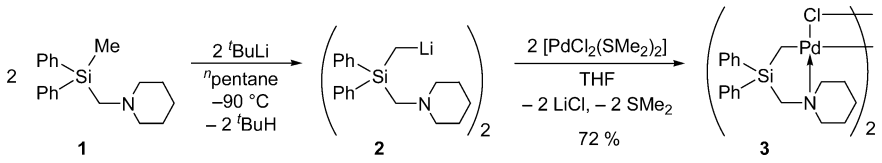
(5) (a) Fuchita, Y.; Nakashima, M.; Hiraki, K.; Kawatani, M. *J. Chem. Soc., Dalton Trans.* **1988**, 785. (b) Eaborn, C.; Hill, M. S.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Chem. Commun.* **2000**, 691. (c) Itami, K.; Kamei, T.; Yoshida, J. *J. Am. Chem. Soc.* **2001**, *123*, 8773.

(6) Maassarani, F.; Pfeffer, M.; Le Borgne, G.; Jastrzebski, J. T. B. H.; van Koten, G. *Organometallics* **1987**, *6*, 1111, and references therein.

(7) Pereira, M. T.; Pfeffer, M.; Rotteveel, M. A. *J. Organomet. Chem.* **1989**, *375*, 139.

(8) [$PdCH_2SiR_3$]: (a) Gutiérrez, E.; Nicasio, M. C.; Paneque, M.; Ruiz, C.; Salazar, V. *J. Organomet. Chem.* **1997**, *549*, 167. (b) Alías, F. M.; Belderraín, T. R.; Carmona, E.; Graiff, C.; Paneque, M.; Tiripicchio, A. *J. Organomet. Chem.* **1999**, *577*, 316. [$PdCH(SiR_3)_2$]: (c) Alías, F. M.; Belderraín, T. R.; Paneque, M.; Poveda, M. L.; Carmona, E.; Valerga, P. *Organometallics* **1997**, *16*, 301. (d) Alías, F. M.; Belderraín, T. R.; Paneque, M.; Poveda, M. L.; Carmona, E.; Valerga, P. *Organometallics* **1998**, *17*, 5620. [$PdC(SiR_3)_3$]: Other structures with the Pd−C−Si moiety: (e) Buchanan, R. M.; Pierpoint, C. G. *Inorg. Chem.* **1979**, *18*, 3608. (f) Maassarani, F.; Pfeffer, M.; Le Borgne, G.; Wehman, E.; van Koten, G. *J. Am. Chem. Soc.* **1984**, *106*, 8002. (g) Onitsuka, K.; Segawa, M.; Takahashi, S. *Organometallics* **1998**, *17*, 4335. (h) Konze, W. V.; Young, V. G., Jr.; Angelici, R. J. *Organometallics* **1998**, *17*, 5275.

Scheme 2



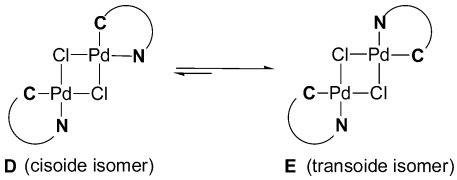
center of compound **3** is also intramolecularly coordinated by the nitrogen center and the carbon center of the corresponding [$CH_2SiPh_2(CH_2NC_5H_{10})$-$\kappa^2C,N$] moiety, forming the palladacycle. The carbon donor center C(1) deviates slightly by 0.21 Å from the square coordination plane (rms deviation of fitted atoms = 0.15 Å). The Pd−C(1) distance of 2.034(2) Å is in the range found for Pd−C(sp^3) single bonds (between 2.00 and 2.19 Å).[10] The difference in the two distances Pd−Cl = 2.329(1) and Pd−Cl′ = 2.491(1) Å reflects the strong electron-donating properties of the (silylmethyl) ligand, giving rise to a high *trans* influence. However, the discrepancy of these distances is similar to those found in other chloro-bridged cyclopalladated dimers with *transoid* geometry,[11] regardless of whether the carbon donor center is part of an aliphatic or aromatic system.[12]

The conformation of the five-membered palladacycle Pd−C(1)−Si−C(14)−N may be described as an envelope with the palladium atom 1.27 Å out of the least-squares plane defined by the other four atoms in the metallacycle (rms deviation of fitted atoms = 0.01 Å). Other palladacycles that may adopt this conformation, such as those with tetrahedral donor atoms (sp^3 carbon and sp^3 nitrogen), are pseudoplanar[12b] or with envelope conformation.[12a,c,f]

The presence of palladium and silicon in a five-membered palladacycle makes the distance Pd−Si = 2.915(1) Å short and the angle Si−C1−Pd = 97.0(1)° small, compared to those found in [(trialkylsilyl)methyl] palladium complexes (3.2 Å and 110° average).[13]

In the ^{1}H NMR spectra, a singlet signal is observed for each methylene group of all the palladacycles described in this work, unless NMR active heterocores, such as ^{31}P, are present in the corresponding complex. This suggests that a ring inversion process, in which the centers Si and C(14) flip from one side to the other, is rapid on the NMR time scale.

Scheme 3



D (cisoide isomer) **E** (transoide isomer)

The ^{1}H and ^{13}C NMR spectra of **3** at room temperature in a $CDCl_3$ solution show the presence of two isomers in a 65:35 ratio, suggested by two singlets observed for each PdCH_2Si and each SiCH_2N methylene group, indicating the presence of a *cisoid* isomer (**D**) and a *transoid* isomer (**E**) (Scheme 3). This is commonly observed for cyclopalladated systems where the alkyl group has a strong *trans* influence.[12a,b,14] A slow equilibrium on the NMR time scale is proposed between the isomers, since the signals of each isomer coalesce in the ^{1}H NMR spectra recorded at higher temperatures. At 70 °C in C_6D_6, only one singlet is detected for the $SiCH_2N$ group.

The ratio between these stereoisomers is very similar in solvents of different polarity ($CDCl_3$, C_6D_6, and thf-d_8 have been used). This observation is surprising, since polar solvents usually give rise to an increase in the ratio of the polar isomer (*cisoid*).[15] Therefore, it is not possible to assign unequivocally the resonance signals in the ^{1}H and ^{13}C{^{1}H} NMR spectra to each isomer. Thus, the major isomer in solution has been tentatively assigned to the *transoid* isomer, which is that found in the crystal structure.

The Si−C stretching absorptions of **3** (and of the other cyclopalladated complexes described in this work) in the IR spectrum are found at 1100 cm^{-1} and in the range between 800 and 700 cm^{-1}, frequencies slightly lower than those previously reported (1243 and 850−820 cm^{-1}) for [(trialkylsilyl)methyl] ligands.[16]

Reactivity of 3 toward Monodentate Ligands. To study the reactivity of complex **3**, a variety of monodentate and bidentate ligands of different geometric and electronic characteristics, neutral or anionic, were chosen. The simplest ligands for reactivity studies of **3** are monodentate neutral ligands, and the expected product should be the result of cleaving the chloro bridges of the starting dimer.[3l,12f,17]

The phosphines PPh_3 and PMe_3 react with **3**, giving the mononuclear complexes of the type [Pd{$CH_2SiPh_2(CH_2NC_5H_{10})$-$\kappa^2C,N$}Cl($PR_3$)] [R = Ph (**4**), Me (**5**)]. The phosphorus center and the carbon center of the ring are

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(10) (a) Maitlis, P. M.; Espinet, P.; Rusell, M. J. H. In *Comprehensive Organometallic Chemistry*, Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford (UK), 1982; Vol. 6, pp 333−334. (b) Reference 4, pp 271−272.

(11) The structures obtained after a search of chloro-bridging complexes in the *Cambridge Crystallographic Database* showed similar discrepancies in the Pd−Cl distances, which seems to indicate that this feature is not associated with the electronic or steric factors of the cylopalladated ligand.

(12) Examples with aliphatic donor atoms: (a) Alyea, E. C.; Dias, S. A.; Ferguson, G.; McAlees, A. J.; McCrindle, R.; Roberts, P. J. *J. Am. Chem. Soc.* **1977**, *99*, 4985. (b) Galli, B.; Gasparrini, F.; Mann, B. E.; Maresca, L.; Natile, G.; Manotti-Lanfredi, A. M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1985**, 1155. (c) Suggs, J. W.; Lee, K. S. *J. Organomet. Chem.* **1986**, *299*, 297. (d) Dupont, J.; Halfen, R. A. P.; Schenato, R.; Berger, A.; Horner, M.; Bortoluzzi, A.; Maichle-Mossmer, C. *Polyhedron* **1996**, *15*, 3465. Examples with aromatic donor atoms: (e) Barr, N.; Dyke, S. F.; Smith, G.; Kennard, C. H. L.; McKee, V. *J. Organomet. Chem.* **1985**, *288*, 109. (f) Zhao, G.; Wang, Q.-G.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1998**, 1241.

(13) A search of the *Cambridge Crystallographic Database* yielded 8 complexes with 16 Pd−C(sp^3)−SiC_3 moieties, with Pd−Si distances 3.054−3.371 Å, mean 3.249 Å; and Pd−C−Si angles 99.5−119.2°, mean 109.9°.

(14) (a) Mutet, C.; Pfeffer, M. *J. Organomet. Chem.* **1979**, *171*, C34. (b) Dehand, J.; Mutet, C.; Pfeffer, M. *J. Organomet. Chem.* **1981**, *209*, 255. (c) Weinberg, E. L.; Hunter, B. K.; Baird, M. C. *J. Organomet. Chem.* **1982**, *240*, 95.

(15) (a) Ladipo, F. T.; Anderson, G. K. *Organometallics* **1994**, *13*, 303. (b) Anderson, G. K.; Cross, R. J.; Manojlovic-Muir, L.; Muir, K. W.; Solomun, T. *J. Organomet. Chem.* **1979**, *170*, 385.

(16) (a) Wozniak, B.; Ruddick, J. D.; Wilkinson, G. *J. Chem. Soc. A* **1971**, 3116. (b) Kelly, R. D.; Young, G. B. *J. Organomet. Chem.* **1989**, *361*, 123.

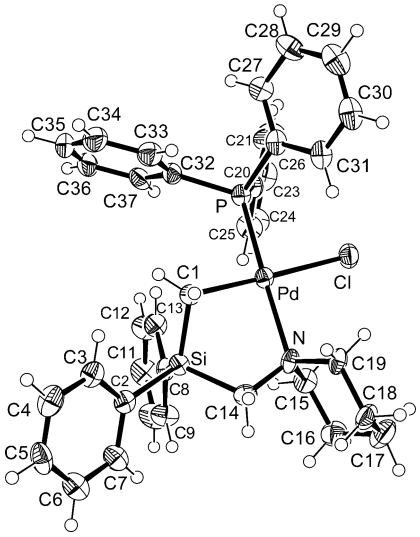


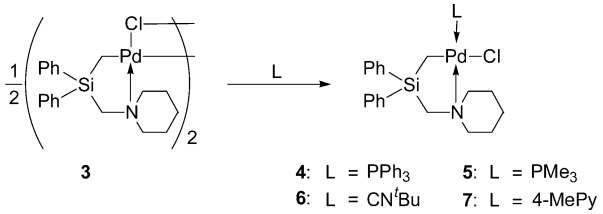
Figure 2. Molecular structure and numbering scheme of compound **4** in the crystal (ORTEP plot, ellipsoids drawn at 50% probability level). Selected distances (Å) and angles (deg): Pd−C(1) 2.067(5), Pd−N 2.212(4), Pd−P 2.238(1), Pd−Cl 2.404(1), Si−C(1) 1.824(4), Pd−Si 3.069(2), C(1)−Pd−N 90.0(2), C(1)−Pd−P 92.9(1), N−Pd−P 175.9(1), C(1)−Pd−Cl 177.7(1), N−Pd−Cl 91.1(1), P−Pd−Cl 86.13-(5), C(1)−Si−C(14) 100.4(2), C(14)−N−Pd 111.4(3), Si−C(1)−Pd 103.9(2), N−C(14)−Si 110.2(3).

coordinated *cis*, which was confirmed by an X-ray diffraction study of **4** (the structure found for **4** and relevant distances and angles are shown in Figure 2). The coordination geometry of the complex is essentially square planar (the phosphorus atom deviates out of a least-squares plane by only 0.05 Å, rms deviation of fitted atoms [Pd, Cl, N, C(1), P] = 0.04 Å), and the Pd−C(1) distance of 2.067(5) Å is again in the usual range found for Pd−C(sp^3) single bonds (between 2.00 and 2.19 Å).[10] The metallacycle shows an envelope conformation, but this time the silicon is the center located 0.86 Å outside of the least-squares plane defined by the other four atoms in the metallacycle (rms deviation of fitted atoms = 0.03 Å), which is a smaller value than for compound **3** (0.86 vs 1.27 Å). The Pd−Si distance [3.069-(2) Å] and the Si−C1−Pd angle [103.9(2)°] are between the values found for **3** and other [(trialkylsilyl)methyl] palladium complexes, as indicated above.[13] The distances and angles are very similar to those found for the structure of the related complex [Pd{CH_2SiMe_2(2-C_5H_4N)-κ^2C,N}Cl(PPh_3)].[5c]

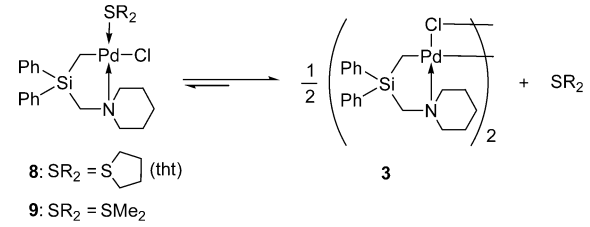
The coordination of the phosphorus center *cis* to the metalated carbon center C(1) is most probably maintained in solution, as the resonance signals of these atoms show low P−H coupling constants in the ^{1}H NMR and no P−C coupling in the $^{13}C\{^1H\}$ NMR spectra at all.[18]

The same *cis* coordination, supported by solid state structural data for **4** and by NMR spectroscopy in the case of the phosphine complexes **4** and **5**, is proposed for the additional complexes obtained after treatment of **3** with neutral monodentate ligands: [Pd{CH_2SiPh_2-($CH_2NC_5H_{10}$)-κ^2C,N}ClL] [L = CN^tBu (**6**), 4-MePy (**7**), tht (**8**), SMe_2 (**9**)]. The fact that this *cis* isomer has always been isolated for cyclometalated complexes of the type [Pd($C-N$)ClL] ($C-N$ = cyclometalated ligand)[19] may be explained considering the higher *trans* influence of the carbon donor ligand and of the incoming ligand L (or the lower *trans* influence of the nitrogen and the chloro ligand). The result is a *cis* configuration, which is in agreement with the *antisymbiotic effect* of the soft palladium(II)center[20] or with what has been more recently defined as the *transphobia effect*.[21]

Scheme 4



Scheme 5



Phosphines and pyridines are usually used to cleave the chloro bridges in cyclometalated systems in order to get more soluble species, since the bridged dimeric chloro complexes are almost insoluble in many solvents and are sometimes difficult to characterize, whereas the monomeric species with phosphines or pyridines are more soluble. We carried out these processes to obtain compounds **6** and **7** (Scheme 4), which are usually described in the chemistry of palladacycles[19] (even though our starting product is readily soluble in most common organic solvents). Stoichiometric amounts of **3** and the ligand CN^tBu or 4-MePy were used for the synthesis of complexes **6** and **7**, but large excesses of tht or SMe_2 are needed to obtain **8** or **9** (Scheme 5). The two latter complexes are stable in solution only when a slight excess of the thioether is present (the ^{1}H NMR spectrum of **8** shows the presence of ca. 10% of **3**, unless an excess of tht is added). These facts must be explained considering the equilibrium shown in Scheme 5, which

(17) (a) Ryabov, A. D.; Kuz'mina, L. G.; Polyakov, V. A.; Kazankov, G. M.; Ryabova, E. S.; Pfeffer, M.; van Eldik, R. *J. Chem. Soc., Dalton Trans.* **1995**, 999. Other recent references: (b) Gül, N.; Nelson, J. H. *Organometallics* **2000**, *19*, 91, and references therein. (c) Liu, X.; Mok, K. F.; Vittal, J. J.; Leung, P.-H. *Organometallics* **2000**, *19*, 3722. (d) Kurita, J.; Usuda, F.; Yasuike, S.; Tsuchiya, T.; Tsuda, Y.; Kiuchi, F.; Hosoi, S. *J. Chem. Soc., Chem Commun.* **2000**, 191, and references therein. (e) Aplin, R. T.; Doucet, H.; Hooper, M. W.; Brown, J. M. *J. Chem. Soc., Chem. Commun.* **1997**, 2097, and references therein.

(18) P−H couplings in aliphatic palladacycles are lower (ca. 3−4 Hz) when the α-C and the phosphine are *cis* than those found when are *trans* (ca. 7−8 Hz); see for example: (a) Constable, A. G.; McDonald, W. S.; Sawkins, L. C.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1980**, 1992. (b) Fuchita, Y.; Hiraki, K.; Matsumoto, Y. *J. Organomet. Chem.* **1985**, *280*, C51. P−C coupling in aliphatic metallacycles is very low (0−13 Hz) when the α-C and the phosphine are *cis*, but much higher (70−80 Hz) when *trans*; see for example ref 14c or: (c) Deeming, A. J.; Rothwell, I. P. *J. Organomet. Chem.* **1981**, *205*, 117.

(19) (a) Omae, I. *Chem. Rev.* **1979**, *79*, 287. (b) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73. (c) Reference 10a, p 321.

(20) Pearson, R. G. *Inorg. Chem.* **1973**, *12*, 712.

(21) (a) Vicente, J.; Arcas, A.; Bautista, D.; Jones, P. G. *Organometallics* **1997**, *16*, 2129. (b) Vicente, J.; Abad, J. A.; Frankland, A. D.; de Arellano, M. C. R. *Chem. Eur. J.* **1999**, *5*, 3066.

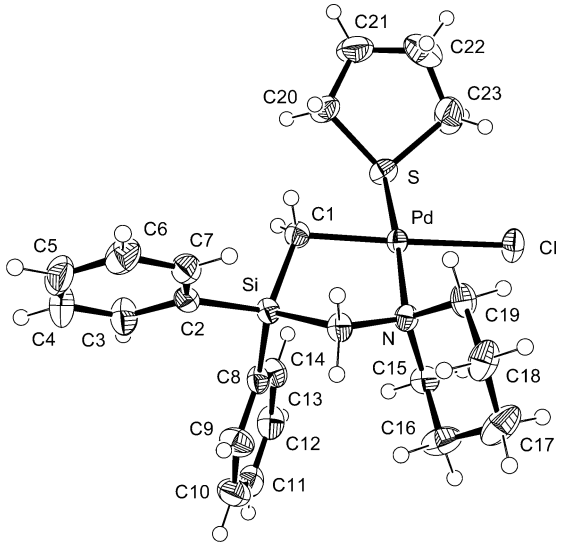


Figure 3. Molecular structure and numbering scheme of compound **8** in the crystal (ORTEP plot, ellipsoids drawn at 50% probability level). Selected distances (Å) and angles (deg): Pd−C(1) 2.062(2), Pd−N 2.175(2), Pd−S 2.2823(7), Pd−Cl 2.4209(7), Si−C(1) 1.840(2), Pd−Si 3.155(2), C(1)−Pd−N 91.26(8), C(1)−Pd−S 86.50(7), N−Pd−S 175.35(5), C(1)−Pd−Cl 177.02(7), N−Pd−Cl 91.66(5), S−Pd−Cl 90.54(2), C(1)−Si−C(14) 100.54(10), C(14)−N−Pd 111.29(13), Si−C(1)−Pd 107.76(11), N−C(14)−Si 110.16(14).

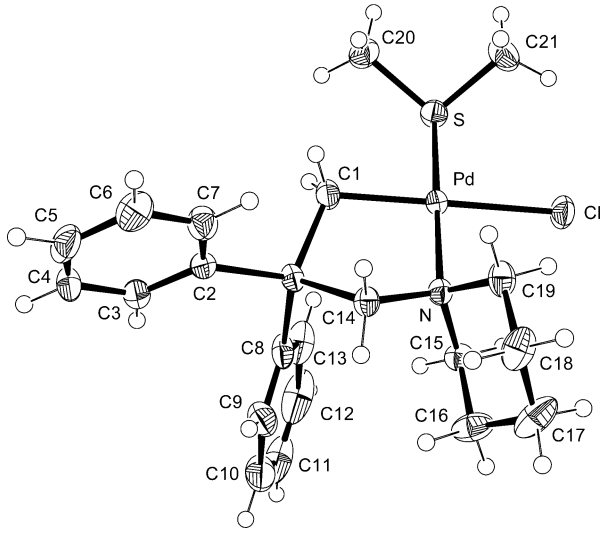


Figure 4. Molecular structure and numbering scheme of compound **9** in the crystal (ORTEP plot, ellipsoids drawn at 50% probability level). Selected distances (Å) and angles (deg): Pd−C(1) 2.051(2), Pd−N 2.161(2), Pd−S 2.2743(5), Pd−Cl 2.4281(5), Si−C(1) 1.837(2), Pd−Si 3.148(2), C(1)−Pd−N 91.59(7), C(1)−Pd−S 88.79(6), N−Pd−S 179.39(4), C(1)−Pd−Cl 174.49(7), N−Pd−Cl 91.76(4), S−Pd−Cl 87.91(2), C(1)−Si−C(14) 101.01(9), C(14)−N−Pd 111.2(1), Si−C(1)−Pd 108.0(1), N−C(14)−Si 109.8(1).

is clearly biased to the right, when stoichiometric amounts of the thioethers are used.[22]

The molecular structures of the thioether complexes **8** and **9** (shown together with relevant distances and angles in Figures 3 and 4) are of particular interest, since they are most probably intermediates in the synthesis of the chloro-bridged dimer **3**,[22] due to the lability of the sulfur ligands, which can be easily replaced during ligand exchange reactions (Schemes 2 and 5). As expected, the sulfur and the metalated carbon center C(1) are coordinated *cis* in both complexes, and the geometry at the central palladium center of both compounds is square planar. For the tht complex **8**, the nitrogen center deviates from a least-squares plane by 0.04 Å (rms deviation of fitted atoms [Pd, Cl, N, C(1), S] = 0.04 Å); the sum of the angles around the palladium center of **8** amounts to 360°. For the dimethylsulfide complex **9**, the metalated carbon center C(1) deviates from a least-squares plane by 0.06 Å (rms deviation of fitted atoms [Pd, Cl, N, C(1), S] = 0.05 Å); the sum of the angles around the palladium center of **9** amounts to 360° as well. The Pd−C distances in both complexes [2.062(2) Å for **8** and 2.051(2) Å for **9**] are equal within the margin of errors, while the Pd−S [2.2823(7) Å for **8** and 2.2743(5) Å for **9**] as well as the Pd−Cl and Pd−N distances are virtually identical. For the envelope conformation of the palladacycle, the following characteristics for least-squares planes were determined: Si deviates from the plane by 0.30 Å, rms deviation of fitted atoms [Pd, C(1), Si, C(14), N] = 0.22 Å for compound **8**; for compound **9**, Si deviates from the plane by 0.29 Å, rms deviation of fitted atoms [Pd, C(1), Si, C(14), N] = 0.21 Å.

Because of the monomeric molecular structures of **8** and **9**, an impression of the mechanism of the formation of the dimer **3** can be gained, which can be regarded as a two-step process: the formation of the corresponding thioether complex first (under substitution of a chloro ligand and extrusion of the first thioether ligand), followed by the dimerization under extrusion of the second thioether ligand.[22]

The attempts to coordinate a second monodentate ligand, starting either from **3** or from the mononuclear complexes **4**−**9**, were not successful, although the coordination of a second PPh_3 ligand has been described for similar cyclopalladated systems.[19]

Thus, these reactions were carried out with $TlBF_4$ in order to favor the removal of the chloro ligand and to obtain cationic species. However, only the 4-MePy ligand gave satisfactory results,[23] yielding [Pd{CH_2SiPh_2-($CH_2NC_5H_{10}$)-κ^2C,N}(4-MePy)$_2$]BF_4 (**10**) (Scheme 6), which was characterized from its analytical, spectroscopic, and crystallographic data (the structure found for **10** and relevant distances and angles are shown in Figure 5). The deviation from the ideal square planar geometry lies between those values found for the structures of **3** and **4**, as the carbon donor atom deviates by 0.12 Å from the least-squares plane of fitted atoms

(22) The thioether complexes **8** and **9** were detected during the first reactions between the organolithium **2** and either *trans*-[$PdCl_2$(tht)$_2$] or *trans*-[$PdCl_2(SMe_2)_2$], which were used as starting materials. Mixtures of **8** and **3** were obtained in the first case, whereas **9** was detected as a byproduct in the synthesis of **3** in the second case before this reaction was finally optimized. In fact, **9** is easily converted into **3** during the workup. Stirring the crude product in an acetone solution favors the formation of **3**, as it is scarcely soluble in this solvent, whereas **9** is soluble. This method for conversion of **9** into **3** has given the best results among others employed. Similar behavior is observed for the tht complex **8**, although the removal of tht is more difficult.

(23) Although **10** is the only cyclopalladated complex isolated when the starting dimer **3** was treated with $TlBF_4$ and 2 equiv of the ligand, the reaction of **3**, $TlBF_4$, and PMe_3 led to a very small amount of the complex *trans*-[$PdPhCl(PMe_3)_2$]. Surprisingly, we have not found any previous reports on this compound in the literature (see Supporting Information for its preparation and spectroscopic data), although a reference of the analogous platinum complex does exist: Arnold, D. P.; Bennett, M. A. *Inorg. Chem.* **1984**, *23*, 2110.

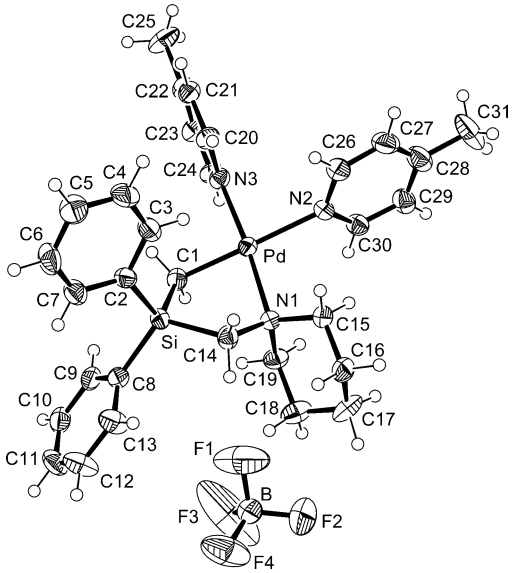
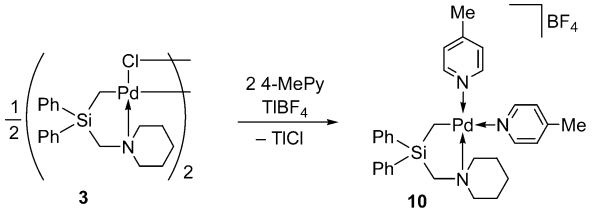


Figure 5. Molecular structure and numbering scheme of compound **10** in the crystal (ORTEP plot, ellipsoids drawn at 50% probability level). Selected distances (Å) and angles (deg): Pd−C(1) 2.050(5), Pd−N(1) 2.124(3), Pd−N(2) 2.180(4), Pd−N(3) 2.046(3), Si−C(1) 1.846(5), Pd−Si 3.091(2), N(3)−Pd−C(1) 88.6(2), N(4)−Pd−N(1) 174.26(14), C(1)−Pd−N(1) 87.2(2), N(4)−Pd−N(2) 87.6(1), C(1)−Pd−N(2) 171.4(2), N(1)−Pd−N(2) 97.2(1), C(1)−Si−C(14) 102.8(2), C(14)−N(1)−Pd 107.1(2), N(1)−C(14)−Si 110.9(3), Si−C(1)−Pd 104.9(2).

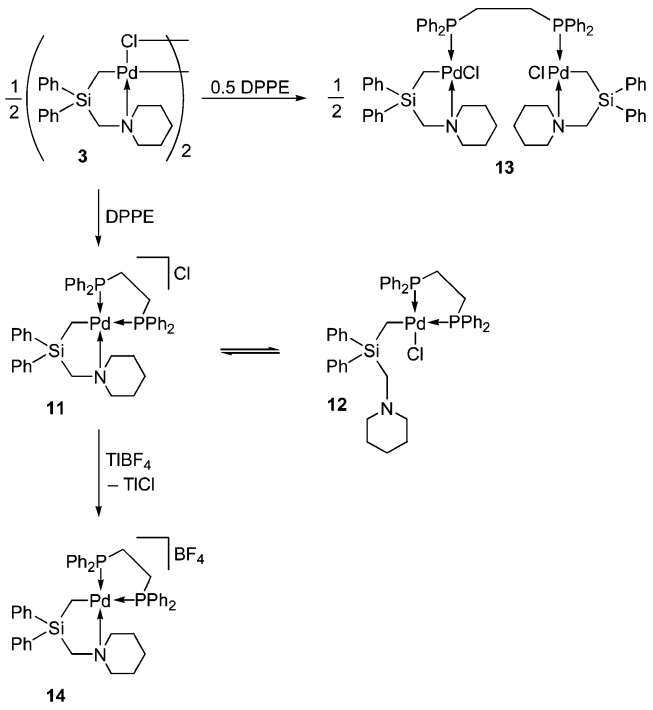
Scheme 6



(rms deviation of fitted atoms [Pd, N(1), N(2), N(3), C(1)] = 0.09 Å). The distance Pd−C(1) = 2.050(5) Å is similar to those found for **3** and **4**. The difference between the distances of both Pd−N bonds 2.180(4) and 2.046(3) Å is similar to that found in **3**, but the lack of geometric constraints in this case, in contrast to **3**, should reflect the strong *trans* influence of the silylmethyl fragment. In the envelope conformation of the five-membered ring, the palladium center is outside of the least-squares plane of the metallacycle, as described for **3**. The Pd−Si distance of 3.091(2) Å and the angle Si−C(1)−Pd of 104.9(2)° are the largest values of their kind of the crystallographically studied complexes in this work.

The lack of other cationic complexes, similar to **10**, may be interpreted considering the known Si−C bond cleavage reactions (mainly in arylsilanes).[24] The removal of the chloro ligand from the palladium coordination sphere by $TlBF_4$ converts the metal center into a strong electrophile, which may facilitate cleavage processes. In fact, precedents on Si−C bond cleavages by palladium salts have been reported, although more drastic reaction conditions than the ones described here had to be applied.[25] Due to the high bond energy of the Si−F bond, the presence of tetrafluoroborate in the reaction mixture may also contribute to decomposition processes.

Scheme 7



Reactivity of 3 toward Bidentate Ligands. Since most of the attempts to introduce two neutral ligands in our system failed, we focused our attention on neutral bidentate ligands, which should give the corresponding cationic complexes. Considerable attention was devoted to cationic palladium complexes with bidentate ligands, mainly because they potentially catalyze the copolymerization of alkenes with carbon monoxide. Diphosphines, such as $Ph_2PCH_2CH_2CH_2PPh_2$ (dppp), or chelating nitrogen donor ligands, such as bipyridines, have shown to be especially efficient in this role.[26] In fact, a palladacycle with dppp has been reported as being highly efficient in the copolymerization process of ethylene with carbon monoxide,[27] and chiral Pd(II) complexes, able to enantioselectively copolymerize propene and carbon monoxide, have also been described.[28] Thus, we investigated the reactivity of **3** toward a diphosphine, such as dppe, which can serve as a model for further studies.

All the processes of compound **3**, involving dppe, are summarized in Scheme 7. The reactions of **3** with dppe depend on the conditions used: the bridging dppe complex $[\{Pd_2[CH_2SiPh_2(CH_2NC_5H_{10})\text{-}\kappa^2C,N]_2Cl_2\}(\mu$-

(24) (a) Elschenbroich, C.; Salzer, A. *Organometallics. A Concise Introduction*, 1st ed.; VCH: Weinheim (Germany), 1989; p 96. (b) Negishi, E.-I. *Organometallics in Organic Synthesis*, Vol. 1 of *General Discussions. Organometallics of Main Group Metals in Organic Synthesis*; Wiley & Sons: Chichester (UK), 1980; Chapter 6.4.1.2. (c) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley: New York, 2000; pp 379−596.

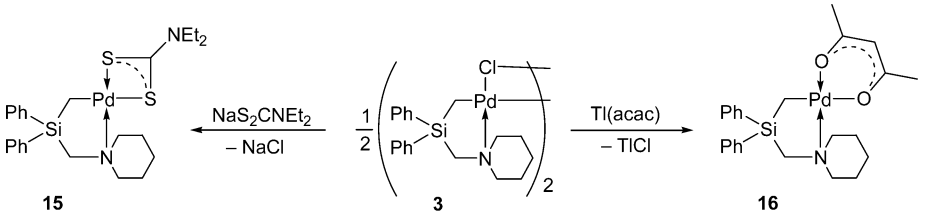
(25) Akhrem, I. S.; Chistovalova, N. M.; Mysov, E. I.; Vol'pin, M. E. *J. Organomet. Chem.* **1974**, *72*, 163.

(26) (a) Sen, A. *Acc. Chem. Res.* **1993**, *26*, 303. (b) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663.

(27) Schwarz, J.; Herdtweck, E.; Herrmann, W. A.; Gardiner, M. G. *Organometallics* **2000**, *19*, 3154.

(28) (a) Nozaki, K.; Sato, N.; Takaya, H. *J. Am. Chem. Soc.* **1995**, *117*, 9911. (b) Nozaki, K.; Sato, N.; Tonomura, Y.; Yasutomi, M.; Takaya, H.; Hyama, T.; Matsubara, T.; Koga, N. *J. Am. Chem. Soc.* **1997**, *119*, 12779.

Scheme 8



dppe)] (**13**) is obtained when a solution of dppe in toluene is slowly added to a toluene solution of an equimolar amount of **3**. However, the chelating dppe complex [Pd{$CH_2SiPh_2(CH_2NC_5H_{10})$-$\kappa^2C,N$}(dppe)]Cl (**11**) is immediately formed when both starting materials are dissolved in dichloromethane in a 2:1 molar ratio (Scheme 7).

The bridging dppe ligand in **13** separates both metal centers, which behave as independent complex fragments, as shown by the similarity of their spectroscopic data and those of compound **4** or **5**. The cationic complex **11** contains a chelating dppe and a chloride as the counterion, but there is evidence from NMR spectroscopy for the transient formation of a species with structure **12** in solution. The reaction of **11** with $TlBF_4$ yields the tetrafluoroborate salt of the same cation, [Pd{$CH_2SiPh_2(CH_2NC_5H_{10})$-$\kappa^2C,N$}(dppe)]$BF_4$ (**14**) (Scheme 7), which does not show any dynamic processes in solution, probably due to the lack of nucleophilicity of the tetrafluoroborate anion. For the molecular structure of compound **14**, a chelate complex is proposed.

For the molecular structure of **11** in the solid state, a chelate complex is proposed as well. In solution, this is supported by the NMR spectra of the complex in $CDCl_3$. The resonance signals of **11**, obtained at a temperature where no dynamic processes, involving **12**, occur (−60 °C), are coincident with those of **14**. The chelate coordination of dppe in **11** and **14** is evident from their $^{31}P\{^1H\}$ NMR spectra, which show two doublets in both cases. A high deshielding is expected for a phosphorus atom of the chelating dppe, as a result of the ring contribution ($\Delta\delta$) of the five-membered Pd−P−C−C−P ring,[14c,29] which explains the deshielding observed for the phosphorus atom *cis* to the metalated carbon center.

On warming to room temperature, the pattern displayed by the protons of the piperidine ring in the ^1H NMR spectra of **11** is very different from that found at lower temperatures or in **14**, as their signals are slightly broad and show resonances at chemical shifts similar to those of free piperidine. This implies an uncoordinated nitrogen atom. The changes in the $^{31}P\{^1H\}$ NMR spectra on warming to room temperature are minor. The addition of chloride ions by PPNCl [bis(triphenylphosphoranylidene)ammonium chloride] to this solution causes the sharpening of the signals of dppe in the ^{31}P NMR and of the (piperidinomethyl) protons in the ^1H NMR spectrum. This observation is in agreement with the equilibrium for **11** proposed in Scheme 7, which is biased to the side of the neutral form in $CDCl_3$ at room temperature and almost completely to the side of the neutral form when an excess of chloride is added by PPNCl.

The partial coordination of the chloride is supported by the electrical conductivity data of 30 $S\cdot cm^2\cdot mol^{-1}$ for the system **11**/**12** in acetone, which is much lower than what is expected for a 1:1 electrolyte (100−140 $S\cdot cm^2\cdot mol^{-1}$ in acetone solution).[30] This is in agreement with the $^{31}P\{^1H\}$ NMR spectra in $(CD_3)_2CO$. The signals observed at −60 °C are assigned to the ionic species, whereas those obtained at room temperature with an excess of chloride in solution are assigned to the neutral complex (see Experimental Section). An averaged $^{31}P\{^1H\}$ NMR spectrum is observed in $(CD_3)_2CO$ at room temperature, but the proposed equilibrium for **11** in Scheme 7 in $(CD_3)_2CO$ is not as biased to the neutral form as in $CDCl_3$. Therefore, the ratio **11**:**12** is greater in a donor solvent such as acetone than in a less polar solvent such as chloroform.[31]

The studies on the reactivity of **3** were completed with two bidentate anionic ligands: acac and diethyldithiocarbamate. These ligands are also being employed to substitute the halogen bridges in palladacycles in order to get more soluble monometallic species.[19]

The reactions of **3** with equimolar amounts of the corresponding sodium and thallium(I) salts gave [Pd{$CH_2SiPh_2(CH_2NC_5H_{10})$-$\kappa^2C,N$}($S_2CNEt_2$)] (**15**) and [Pd{$CH_2SiPh_2(CH_2NC_5H_{10})$-$\kappa^2C,N$}(acac)] (**16**) (Scheme 8). The first compound was studied by X-ray diffraction methods (the structure found for **15** and relevant distances and angles are shown in Figure 6).

The sulfur center S(1) deviates by only 0.07 Å from the essentially square planar coordination plane (rms deviation of fitted atoms [Pd, S(1), S(2), N, C(1)] = 0.05 Å). The Pd−C(1) distance of 2.074(2) Å is similar to those found in the other structures described. The difference between the two Pd−S distances of compound **15**, Pd−S(1) *cis* and Pd−S(2) *trans* to the metalated carbon center C(1) [2.408(1) and 2.280(1) Å], is similar to the corresponding differences found in compound **3** or **10**, reflecting again the strong *trans* influence of the [(aminomethyl)silylmethyl] fragment. These distances are almost identical to those found when a chelating dithiocarbamato ligand is coordinated *trans* to two ligands of very different *trans* influence, such as an alkyl group and an alkene.[32] The palladium center is out of the least-squares plane for the metallacycle by 1.19 Å (rms deviation of fitted atoms [Pd, C(1), Si, C(14), N] = 0.07 Å), as observed for **3** and **10**. The deviation in this

(29) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.
(30) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.
(31) A possible alternative process to the replacement of the nitrogen donor center by the chloride would be the substitution of the chloride by one of the phosphorus atoms of dppe. This can be discarded from the $^{31}P\{^1H\}$ NMR data: a process involving the decoordination of one of the phosphorus centers would give rise to severe signal broadening or large changes in the chemical shifts of both doublets. In fact, strong shielding should be expected for both phosphorus resonance signals if the dppe changes from chelate mode to monodentate mode, as the ring contribution would not be effective. The doublet displayed by the uncoordinated phosphorus atom would also be very shielded, as it should show resonance near free dppe ($\delta = -13.3$).
(32) Bailey, P. M.; Taylor, S. H.; Maitlis, P. M. *J. Am. Chem. Soc.* **1978**, *100*, 4711.

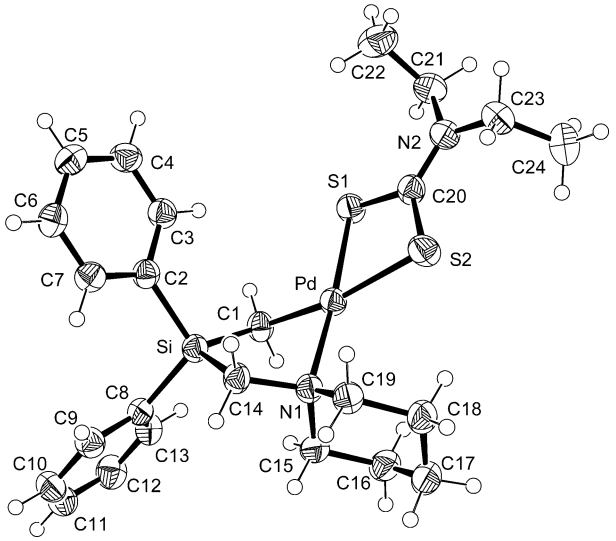


Figure 6. Molecular structure and numbering scheme of compound **15** in the crystal (ORTEP plot, ellipsoids drawn at 50% probability level). Selected distances (Å) and angles (deg): Pd−C(1) 2.074(2), Pd−N(1) 2.155(2), Pd−S(1) 2.280(1), Pd−S(2) 2.408(1), Si−C(1) 1.843(2), Pd−Si 3.020(1), N(2)−C(20) 1.324(3), S(1)−C(20) 1.724(3), S(2)−C(20) 1.712(3), C(1)−Pd−N(1) 87.6(1), C(1)−Pd−S(1) 92.9(1), N(1)−Pd−S(1) 174.21(5), C(1)−Pd−S(2) 168.05(7), N(1)−Pd−S(2) 104.35(6), S(1)−Pd−S(2) 75.12(3), C(1)−Pd−Si 36.82(7), N(1)−Pd−Si 62.52(5), S(1)−Pd−Si 115.07(2), S(2)−Pd−Si 149.84(3), C(1)−Si−C(14) 105.2(1), C(14)−N(1)−Pd 102.7(1), C(20)−S(1)−Pd 88.0(1), C(20)−S(2)−Pd 84.2(1), N(1)−C(14)−Si 109.2(2).

case is the second highest after the one found for **3**. The C−S and C−N bond lengths as well as the S−Pd−S or S−C−S angles found in the dithiocarbamate ligand are similar to those reported for other dithiocarbamatopalladium complexes.[33]

Conclusions and Outlook

The palladacycle formed by the [diphenyl(piperidinomethyl)silylmethyl] ligand and different palladium complex fragments remains intact during reactions in which bridging chloro ligands are cleaved by neutral ligands or substituted by anionic bidentate ligands. However, only the complex with two 4-methylpyridine ligands could be obtained during the attempts to obtain cationic complexes with monodentate neutral ligands, whereas a process involving Pd−N cleavage is detected in solution of the complex with a neutral bidentate ligand, such as dppe. Further studies on the reactivity of the chloro-bridged dimer are currently in progress.

X-ray structural analyses of compounds representative of the main structural types show the strong *trans* influence of the [(piperidinomethyl)silylmethyl] fragment, regardless of neutral or cationic complexes. The palladacycle adopts an envelope conformation in all the structures, and the presence of palladium and silicon in a five-membered palladacycle makes the Pd−Si distances short and the Si−C−Pd angles small, when compared with those found in terminal [(trialkylsilyl)methyl] palladium complexes. Furthermore, a shortening of the Si−C bonds between silicon and the metalated carbon center [values for Si−C(1) between 1.824(4) and 1.855(3) Å for all four different Si−C(1) bonds discussed in this paper compared to 1.914(9) Å in a corresponding nonmetalated silane][2a] is an indicator for the stabilizing effect of silicon centers on metalated α-carbon centers.

It is of great interest to study reactions between the highly enantiomerically enriched lithium alkyls of type **B** with palladium(II) compounds in order to obtain highly enantiomerically enriched palladium compounds of type **C** (Scheme 1), which could be valuable systems, e.g., for the stereoselective formation of C−C bonds or insertion reactions in the Pd−C bond. First preliminary results on corresponding starting compounds have been published as a review within the scope of the interdisciplinary research unit SFB347 (Selective Reactions of Metal-activated Molecules) at the University of Würzburg.[1a]

Experimental Section

General Comments. Infrared spectra [KBr pellets, 4000−400 cm^{-1}]: Perkin-Elmer 1720X. ^1H NMR [solvent $CDCl_3$; internal standard $CHCl_3$ ($\delta = 7.20$)]: Bruker AC-300 or ARX-300 (300.13 MHz). $^{31}P\{^1H\}$ NMR [external standard 85% aqueous H_3PO_4 ($\delta = 0$)]: Bruker AC-300 or ARX-300 (121.49 MHz). ^{13}C NMR [solvent and internal standard $CDCl_3$ ($\delta = 77.00$)]: Bruker ARX-300 (75.78 MHz). Assignment of the ^{13}C NMR data was supported by DEPT experiments and the relative intensities of the resonance signals. $^{29}Si\{^1H\}$ and 2D $^{29}Si-^1H$ HMBC NMR [solvent $CDCl_3$; internal standard TMS ($\delta = 0$)]: Bruker DRX-300 (59.63 MHz). Microanalyses: Perkin-Elmer 2400B microanalyzer, Química Inorgánica, Facultad de Ciencias, Valladolid. Electrical conductivity [ca. 5×10^{-4} M solutions; range of molar conductivity for 1:1 electrolytes = 100−140 $S \cdot cm^2 \cdot mol^{-1}$ in acetone]:[30] Crison 522. All reactions were carried out under oxygen-free and dried dinitrogen following conventional Schlenk techniques. The solvents were dried according to common procedures. $[PdCl_2(SMe_2)_2]$ was obtained as described for the tht complex,[34] $TlBF_4$,[35] and Tl(acac)[36] as reported (CAUTION: Tl(I) derivatives are toxic and should be handled with care). The rest of the reactants were obtained from usual commercial suppliers.

Synthesis of $Ph_2Si(CH_2Li)(CH_2NC_5H_{10})$ (2). In a Schlenk flask, a solution of 550 mg (1.86 mmol) of $Ph_2SiMe(CH_2NC_5H_{10})$ (**1**) in *n*-pentane (4 mL) was cooled to −90 °C, and 1.09 mL of *t*-BuLi (in *n*-pentane, $c = 1.7$ mol·L^{-1}) (1.86 mmol) was added. After slowly warming the yellow mixture to room temperature, **2** precipitated as an off-white solid. The mixture was stirred for one additional hour before the solvent was removed in vacuo. The solid was immediately used for the synthesis of compound **3**. To isolate **2** as yellow single crystals, the solution has to be warmed from −90 to −30 °C and kept for 6 h at this temperature, yielding **2** (504 mg, 1.67 mmol, 90%) (after washing with *n*-pentane and drying in vacuo).

Synthesis of $[Pd\{CH_2SiPh_2(CH_2NC_5H_{10})-\kappa^2C,N\}(\mu\text{-}Cl)]_2$ (3). Solid *trans*-$[PdCl_2(SMe_2)_2]$ (2.63 g, 8.77 mmol) was added to a freshly prepared solution of **2** (2.64 g, 8.77 mmol) in thf (88 mL), cooled to −78 °C. The mixture was stirred for 5 h and was allowed to warm to room temperature. Two drops of water were added to hydrolyze a potential excess of organo-

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lithium reagent. The volatile components were removed in vacuo, and the residue was successively washed with *n*-hexane (3 × 20 mL) and acetone (3 × 10 mL) and then extracted with CH_2Cl_2 (50 mL) and filtered on dry Celite. *n*-Hexane (ca. 30 mL) was added to the filtrate, which was concentrated and cooled to −20 °C to give a yellow microcrystalline solid, which was washed with *n*-hexane (3 × 10 mL) and dried in vacuo. The *n*-hexane and acetone extracts were subjected to the same treatment after removing the volatile components in vacuo and extracting with CH_2Cl_2. Yield: 2.74 g (72%) of **3**. ^{1}H NMR: δ 7.67 (m, C_6H_5, 4H, *cisoid* and *transoid*), 7.34 (m, C_6H_5, 6H, *cisoid* and *transoid*), 3.37 (m, NC_5H_{10}, 2H, *cisoid* and *transoid*), 3.00 (s, $SiCH_2N$, 2H, *transoid*), 2.95 (s, $SiCH_2N$, 2H, *cisoid*), 2.47 (m, NC_5H_{10}, 2H, *cisoid*), 2.36 (m, NC_5H_{10}, 2H, *transoid*), 1.8−1.2 (br m, NC_5H_{10}, 6H, *cisoid* and *transoid*), 1.49 (s, $PdCH_2Si$, 2H, *transoid*), 1.41 (s, $PdCH_2Si$, 2H, *cisoid*). Ratio *transoid*/*cisoid* = 65:35. ^{13}C{^{1}H} NMR: δ 136.1 (s, Si-*i*-C_6H_5), 134.7 (s, Si-*o*-C_6H_5), 129.3 (s, Si-*p*-C_6H_5), 127.9 (s, Si-*m*-C_6H_5), 62.4 (s, $NCH_2CH_2CH_2$, *transoid*), 61.7 (s, $NCH_2CH_2CH_2$, *cisoid*), 55.2 (s, NCH_2Si, *transoid*), 53.9 (s, NCH_2Si, *cisoid*), 23.1 (s, $NCH_2CH_2CH_2$), 22.5 (s, $NCH_2CH_2CH_2$, *transoid*), 21.6 (s, $NCH_2CH_2CH_2$, *cisoid*), 5.2 (s, $PdCH_2Si$, *transoid*), 2.0 (s, NCH2CH2CH2, *cisoid*). ^{29}Si{1H} NMR: δ 0.65. IR: 3045 w, 3004 w, 2941 m, 2861 w, 1441 w, 1427 s, 1378 w, 1111 s, 1037 w, 864 w, 836 w, 792 w, 766 s, 752 s, 736 s, 722 s, 702 s, 518 w, 515 w, 488 m, 462 w, 428 w. Anal. Calcd for $C_{38}H_{48}Cl_2N_2Pd_2Si_2$: C, 52.30; H, 5.54; N, 3.21. Found: C, 52.44; H, 5.34; N, 3.27.

Synthesis of [Pd{*CH*$_2$SiPh$_2$(CH$_2$*N*C$_5$H$_{10}$)-κ^2*C,N*}Cl(PPh$_3$)] (4). Solid PPh_3 (105 mg, 400 μmol) was added to a solution of **3** (175 mg, 200 μmol) in CH_2Cl_2 (15 mL), and the solution was stirred for 1 h. *n*-Hexane (10 mL) was added to this solution, which was then concentrated and cooled to −20 °C. Colorless crystals were obtained and isolated, washed with *n*-hexane (3 × 3 mL), and dried in vacuo to give 246 mg (88%) of **4**. ^{31}P-{^{1}H} NMR: δ 37.8 (s). ^{1}H NMR: δ 7.6 (m, C_6H_5, 6H), 7.4 (m, C_6H_5, 4H), 7.2 (m, C_6H_5, 15H), 3.93 (m, NC_5H_{10}, 2H), 2.87 (d, $^4J_{P,H}$ = 1.5 Hz, $SiCH_2N$, 2H), 2.49 (m, NC_5H_{10}, 2H), 1.7−1.4 (br m, NC_5H_{10}, 6H), 0.57 (d, $^3J_{P,H}$ = 3.5 Hz, $PdCH_2Si$, 2H). ^{13}C-{^{1}H} NMR: δ 136.9 (s, Si-*i*-C_6H_5), 134.6 (d, $^2J_{C,P}$ = 12 Hz, P-*o*-C_6H_5), 134.5 (s, Si-*o*-C_6H_5), 132.1 (d, $^1J_{C,P}$ = 51 Hz, P-*i*-C_6H_5), 130.1 (s, P-*p*-C_6H_5), 129.1 (s, Si-*p*-C_6H_5), 127.9 (d, $^3J_{C,P}$ = 11 Hz, P-*m*-C_6H_5), 127.7 (s, Si-*m*-C_6H_5), 59.5 (s, $NCH_2CH_2CH_2$), 49.3 (s, NCH_2Si), 23.5 (s, $NCH_2CH_2CH_2$), 21.5 (s, $NCH_2CH_2CH_2$), 11.4 (s, $PdCH_2Si$). ^{29}Si{^{1}H} NMR: δ −0.07. IR: 3052 w, 2933 m, 2859 w, 1482 m, 1434 s, 1404 w, 1097 s, 800 w, 781 w, 737 s, 698 vs, 536 s, 513 m, 499 m, 426 w. Anal. Calcd for $C_{37}H_{39}ClNPPdSi$: C, 63.61; H, 5.63; N, 2.00. Found: C, 63.43; H, 5.48; N, 2.27.

Synthesis of [Pd{*CH*$_2$SiPh$_2$(CH$_2$*N*C$_5$H$_{10}$)-κ^2*C,N*}Cl(PMe$_3$)] (5). A solution of PMe_3 (CAUTION: PMe_3 is potentially dangerous; it should be handled only in a well-ventilated hood) in thf (c = 1.0 mol·L^{-1}, 200 μL, 200 μmol) was added to a solution of **3** (87.3 mg, 100 μmol) in CH_2Cl_2 (15 mL), and the mixture was stirred for 1 h. *n*-Hexane (10 mL) was added to this solution, which was concentrated and cooled to −20 °C. Colorless crystals were obtained, isolated, washed with *n*-hexane (3 × 3 mL), and dried in vacuo to give 44.1 mg (43%) of **5**. ^{31}P{^{1}H} NMR: δ −0.7 (s). ^{1}H NMR: δ 7.57 (m, C_6H_5, 4H), 7.30 (m, C_6H_5, 6H), 3.65 (m, NC_5H_{10}, 2H), 2.79 (d, $^4J_{P,H}$ = 1 Hz, $SiCH_2N$, 2H), 2.35 (m, NC_5H_{10}, 2H), 1.6−1.2 (br m, NC_5H_{10}, 6H), 1.43 (d, $^2J_{P,H}$ = 11 Hz, PCH_3, 9H), 0.55 (d, $^3J_{P,H}$ = 4 Hz, $PdCH_2Si$, 2H). ^{13}C{^{1}H} NMR: δ 137.0 (s, Si-*i*-C_6H_5), 134.5 (s, Si-*o*-C_6H_5), 129.1 (s, Si-*p*-C_6H_5), 127.7 (s, Si-*m*-C_6H_5), 59.3 (s, $NCH_2CH_2CH_2$), 49.6 (s, NCH_2Si), 23.4 (s, $NCH_2CH_2CH_2$), 21.5 (s, $NCH_2CH_2CH_2$), 16.6 (d, $^1J_{C,P}$ = 34 Hz, PCH_3), 2.8 (s, $PdCH_2Si$). ^{29}Si{^{1}H} NMR: δ 0.14. IR: 3063 w, 2963 w, 2841 w, 2805 w, 1484 w, 1427 m, 1415 w, 1377 w, 1303 w, 1285 w, 1175 w, 1111 m, 1048 w, 961 s, 855 w, 793 w, 764 s, 748 s, 735 s, 701 s, 546 w, 496 w, 484 w. Anal. Calcd for $C_{22}H_{33}ClNPPdSi$: C, 51.57; H, 6.49; N, 2.73. Found: C, 51.33; H, 6.52; N, 2.98.

Synthesis of [Pd{*CH*$_2$SiPh$_2$(CH$_2$*N*C$_5$H$_{10}$)-κ^2*C,N*}Cl(CN^{t}Bu)] (6). CN^{t}Bu (34.9 mg, 420 μmol) was added to a solution of **3** (175 mg, 200 μmol) in CH_2Cl_2 (30 mL), and the mixture was stirred for 5 min. The solution was filtered on alumina IV, the volatile components were removed in vacuo, and the residue was washed with *n*-hexane (3 × 5 mL) and vacuum-dried to give 116 mg (56%) of **6** as a colorless solid, which was recrystallized from CH_2Cl_2/*n*-hexane at −20 °C. ^{1}H NMR: δ 7.56 (m, C_6H_5, 4H), 7.31 (m, C_6H_5, 6H), 3.70 (m, NC_5H_{10}, 2H), 2.82 (s, $SiCH_2N$, 2H), 2.42 (m, NC_5H_{10}, 2H), 1.7−1.3 (br m, NC_5H_{10}, 6H), 1.45 (s, CCH_3, 9H), 0.99 (s, $PdCH_2Si$, 2H). ^{13}C{^{1}H} NMR: δ *C*N^{t}Bu not observed, 136.1 (s, Si-*i*-C_6H_5), 134.5 (s, Si-*o*-C_6H_5), 129.3 (s, Si-*p*-C_6H_5), 127.8 (s, Si-*m*-C_6H_5), 59.3 (s, $NCH_2CH_2CH_2$), 58.0 (s, $CNC(CH_3)_3$), 49.9 (s, NCH_2-Si), 30.1 (s, $CNC(CH_3)_3$), 23.1 (s, $NCH_2CH_2CH_2$), 20.7 (s, $NCH_2CH_2CH_2$), −1.0 (s, $PdCH_2Si$). ^{29}Si{1H} NMR: δ 1.47. IR: 3066 w, 2932 m, 2204 s, 1455 w, 1427 m, 1401 w, 1385 w, 1373 w, 1196 m, 1110 m, 866 w, 736 m, 701 m, 544 w, 503 w, 491 w. Anal. Calcd for $C_{24}H_{33}ClN_2PdSi$: C, 55.49; H, 6.40; N, 5.39. Found: C, 55.28; H, 6.23; N, 5.48.

Synthesis of [Pd{*CH*$_2$SiPh$_2$(CH$_2$*N*C$_5$H$_{10}$)-κ^2*C,N*}Cl(4-MePy)] (7). 4-MePy (75.0 mg, 800 μmol) was added to a solution of **3** (349 mg, 400 μmol) in CH_2Cl_2 (20 mL), and the mixture was stirred for 1 h. *n*-Hexane (20 mL) was added to the solution, which was concentrated and cooled to −20 °C. Yellow crystals were obtained and isolated, washed with *n*-hexane (3 × 3 mL), and dried in vacuo to give 263 mg (62%) of **7**. ^{1}H NMR: δ 8.50 (d, J = 5.5 Hz, *H*2 of MePy, 2H), 7.61 (m, C_6H_5, 4H), 7.31 (m, C_6H_5, 6H), 7.00 (d, J = 5.5 Hz, *H*3 of MePy, 2H), 3.85 (m, NC_5H_{10}, 2H), 2.95 (s, $SiCH_2N$, 2H), 2.55 (m, NC_5H_{10}, 2H), 2.28 (s, $NC_5H_4CH_3$, 3H), 1.8−1.3 (br m, NC_5H_{10}, 6H), 1.03 (s, $PdCH_2Si$, 2H). ^{13}C{^{1}H} NMR: δ 152.4 (s, *o*-$NC_5H_4CH_3$), 148.9 (s, *p*-$NC_5H_4CH_3$), 136.4 (s, Si-*i*-C_6H_5), 134.4 (s, Si-*o*-C_6H_5), 129.1 (s, Si-*p*-C_6H_5), 127.7 (s, Si-*m*-C_6H_5), 125.5 (s, *m*-$NC_5H_4CH_3$), 61.4 (s, $NCH_2CH_2CH_2$), 52.6 (s, NCH_2-Si), 23.0 (s, $NCH_2CH_2CH_2$), 21.2 (s, $NCH_2CH_2CH_2$), 20.8 (s, $NC_5H_4CH_3$), 5.9 (s, $PdCH_2Si$). ^{29}Si{1H} NMR: δ 0.85. IR: 3064 w, 3042 w, 3007 w, 2934 m, 2856 m, 1618 m, 1503 w, 1455 m, 1427 m, 1372 w, 1258 w, 1227 w, 1213 w, 1154 w, 1110 m, 1072 w, 1029 w, 998 w, 948 w, 867 m, 806 m, 782 m, 735 s, 702 s, 618 w, 549 s, 502 s, 465 w, 425 w. Anal. Calcd for $C_{25}H_{31}ClN_2PdSi$: C, 56.71; H, 5.90; N, 5.29. Found: C, 56.57; H, 5.87; N, 5.13.

Synthesis of [Pd{*CH*$_2$SiPh$_2$(CH$_2$*N*C$_5$H$_{10}$)-κ^2*C,N*}Cl(tht)] (8). Tht (1.06 g, 12.0 mmol) was added to a mixture of **3** (262 mg, 300 μmol) in acetone (15 mL). The mixture was stirred for 1 h until a clear solution was obtained. *n*-Hexane (10 mL) was added to this solution, which was then concentrated and cooled to −20 °C. Yellow crystals were obtained and isolated, washed with *n*-hexane (3 × 3 mL), and dried in vacuo to give 195 mg (62%) of **8**. ^{1}H NMR: δ 7.60 (m, C_6H_5, 4H), 7.32 (m, C_6H_5, 6H), 3.84 (m, NC_5H_{10}, 2H), 3.13 (br, *H*2 of tht, 4H), 2.90 (s, $SiCH_2N$, 2H), 2.51 (m, NC_5H_{10}, 2H), 1.99 (m, *H*3 of tht, 4H), 1.8−1.4 (br m, NC_5H_{10}, 6H), 0.92 (s, $PdCH_2Si$, 2H). ^{13}C{^{1}H} NMR: δ 136.0 (s, Si-*i*-C_6H_5), 134.5 (s, Si-*o*-C_6H_5), 129.2 (s, Si-*p*-C_6H_5), 127.8 (s, Si-*m*-C_6H_5), 60.8 (s, $NCH_2CH_2CH_2$), 51.2 (s, NCH_2Si), 37.4 (s, SCH_2CH_2), 29.7 (s, SCH_2CH_2), 23.1 (s, NCH_2-CH_2CH_2), 21.2 (s, $NCH_2CH_2CH_2$), 6.7 (s, $PdCH_2Si$). ^{29}Si{^{1}H} NMR: δ 0.44. IR: 3062 w, 2929 m, 2858 w, 1427 w, 1407 w, 1386 m, 1354 m, 1302 w, 1157 w, 1104 m, 1030 w, 840 w, 803 m, 784 m, 749 m, 738 s, 698 s, 544 w, 504 w, 491 w. Anal. Calcd for $C_{23}H_{32}ClNPdSSi$: C, 52.67; H, 6.15; N, 2.67. Found: C, 52.73; H, 5.98; N, 2.43.

Synthesis of [Pd{*CH*$_2$SiPh$_2$(CH$_2$*N*C$_5$H$_{10}$)-κ^2*C,N*}Cl(SMe$_2$)] (9). SMe_2 (240 mg, 4.00 mmol) was added to a suspension of **3** (175 mg, 200 μmol) in acetone (30 mL). The solution, which was immediately formed, was stirred for 5 min. *n*-Hexane (30 mL) was added to this solution, which was concentrated and cooled to −20 °C. Yellow crystals were obtained and isolated, washed with *n*-hexane (3 × 3 mL), and dried in vacuo to give 108 mg (54%) of **9**. ^{1}H NMR: δ 7.57 (m, C_6H_5, 4H), 7.31 (m,

C_6H_5, 6H), 3.82 (m, NC_5H_{10}, 2H), 2.91 (s, $SiCH_2N$, 2H), 2.50 (m, NC_5H_{10}, 2H), 2.35 (s, SCH_3, 6H), 1.7−1.3 (br m, NC_5H_{10}, 6H), 1.00 (s, $PdCH_2Si$, 2H). $^{13}C\{^1H\}$ NMR: δ 136.0 (s, Si-*i*-C_6H_5), 134.3 (s, Si-*o*-C_6H_5), 129.2 (s, Si-*p*-C_6H_5), 127.7 (s, Si-*m*-C_6H_5), 60.8 (s, $NCH_2CH_2CH_2$), 51.3 (s, NCH_2Si), 23.0 (s, $NCH_2CH_2CH_2$), 22.8 (s, SCH_3), 21.3 (s, $NCH_2CH_2CH_2$), 7.0 (s, $PdCH_2Si$). $^{29}Si\{^1H\}$ NMR: δ 0.07. IR: 3062 w, 3012 w, 2976 m, 2922 m, 2867 m, 2845 m, 1455 m, 1427 m, 1411 w, 1355 w, 1325 w, 1300 w, 1234 w, 1156 w, 1104 m, 1029 m, 980 m, 947 w, 911 w, 867 m, 840 m, 802 w, 785 m, 738 s, 696 s, 617 w, 543 m, 503 w, 493 w. Anal. Calcd for $C_{21}H_{30}ClNPdSSi$: C, 50.60; H, 6.07; N, 2.81. Found: C, 50.62; H, 5.95; N, 2.62.

Synthesis of [Pd{*C*H_2SiPh$_2$(CH_2*N*C_5H_{10})-κ^2*C,N*}(4-MePy)$_2$]BF$_4$ (10). A Schlenk flask was successively charged with **3** (87.3 mg, 100 μmol), CH_2Cl_2 (10 mL), 4-MePy (7.40 mg, 400 μmol), and $TlBF_4$ (58.2 mg, 200 μmol), and the mixture was stirred for 16 h. The mixture was then filtered and concentrated, and Et_2O was added to the filtrate. After cooling to −20 °C, a white microcrystalline solid was obtained. It was isolated, washed with *n*-hexane (3 × 3 mL), and dried in vacuo to give 93.0 mg (69%) of **10**. ^1H NMR: δ 8.68 (d, J = 6 Hz, *H*2 of MePy, 2H), 8.30 (d, J = 6 Hz, *H*2 of MePy, 2H), 7.61 (m, C_6H_5, 4H), 7.37 (m, C_6H_5, 6H), 7.23 (d, J = 6 Hz, *H*3 of MePy, 2H), 7.03 (d, J = 6 Hz, *H*3 of MePy, 2H), 3.16 (s, $SiCH_2N$, 2H), 3.03 (m, NC5H_{10}, 2H), 2.65 (m, NC_5H_{10}, 2H), 2.27 (s, $NC_5H_4CH_3$, 3H), 2.21 (s, $NC_5H_4CH_3$, 3H), 1.61 (m, NC_5H_{10}, 2H), 1.33 (m, NC_5H_{10}, 4H), 0.99 (s, $PdCH_2Si$, 2H). $^{13}C\{^1H\}$ NMR: δ 151.2 (s, *o*-$NC_5H_4CH_3$), 150.5 (s, *p*-$NC_5H_4CH_3$), 150.4 (s, *p*-$NC_5H_4CH_3$), 149.5 (s, *o*-$NC_5H_4CH_3$), 136.0 (s, Si-*i*-C_6H_5), 134.4 (s, Si-*o*-C_6H_5), 129.5 (s, Si-*p*-C_6H_5), 128.1 (s, Si-*m*-C_6H_5), 127.2 (s, *m*-$NC_5H_4CH_3$), 126.9 (s, *m*-$NC_5H_4CH_3$), 61.9 (s, $NCH_2CH_2CH_2$), 54.2 (s, NCH_2Si), 22.7 (s, $NCH_2CH_2CH_2$), 21.1 (s, $NCH_2CH_2CH_2$), 21.0 (s, $NC_5H_4CH_3$), 20.8 (s, $NC_5H_4CH_3$), 3.9 (s, $PdCH_2Si$). $^{29}Si\{^1H\}$ NMR: δ −0.29. IR: 3065w, 2945 m, 2871 w, 1617 m, 1504 w, 1428 m, 1385 w, 1211 w, 1110 s, 1068 s br, 869 w, 818 m, 763 m, 738 m, 704 m, 503 w. Anal. Calcd for $C_{31}H_{38}BF_4N_3PdSi$: C, 55.25; H, 5.68; N, 6.23. Found: C, 55.17; H, 5.42; N, 6.10. Conductivity: Λ_M (Me_2CO): 100 S·cm^2·mol^{-1}.

Synthesis of [Pd{*C*H_2SiPh$_2$(CH_2*N*C_5H_{10})-κ^2*C,N*}(dppe)]Cl (11). Dppe (79.7 mg, 200 μmol) was added to a solution of **3** (87.3 mg, 100 μmol) in CH_2Cl_2 (10 mL), and the solution was stirred for 5 min. All volatile components were removed in vacuo, and the residue was washed with Et_2O (3 × 3 mL) to give 127 mg (76%) of **11** as a colorless solid, which was recrystallized from thf/*n*-hexane at −20 °C. $^{31}P\{^1H\}$ NMR: δ 58.4 (d, $^3J_{P,P}$ = 20 Hz), 42.7 (br d, $^3J_{P,P}$ = 20 Hz). $^{31}P\{^1H\}$ NMR (−60 °C): δ 59.3 (d, $^3J_{P,P}$ = 19 Hz), 44.3 (d, $^3J_{P,P}$ = 20 Hz). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, after dissolving the solid at −60 °C]: δ 64.5 (d, $^3J_{P,P}$ = 19 Hz), 46.2 (d, $^3J_{P,P}$ = 19 Hz). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, excess of PPNCl]: δ 60.5 (d, $^3J_{P,P}$ = 25 Hz), 36.5 (d, $^3J_{P,P}$ = 25 Hz). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$]: δ 60.3 (d, $^3J_{P,P}$ = 23 Hz), 39.0 (br d, $^3J_{P,P}$ = 23 Hz. ^1H NMR: δ 7.4 (br m, C_6H_5, 20H), 7.33 (m, C_6H_5, 2H), 7.21 (m, C_6H_5, 8H), 2.92 (s, $SiCH_2N$, 2H), 2.82 (br, NC_5H_{10}, 4H), 2.33 (m, PCH_2, 4H), 1.29 (m, NC_5H_{10}, 4H), 0.91 (m, 2H of $PdCH_2Si$, and 2H of NC_5H_{10}). ^1H NMR (−60 °C): δ 7.77 (m, C_6H_5, 1H), 7.5−7.1 (m, C_6H_5, 29H), 2.96 (m, NC_5H_{10}, 2H), 2.83 (s, $SiCH_2N$, 2H), 2.64 (m, NC_5H_{10}, 2H), 2.18 (m, PCH_2, 4H), 1.64 (m, NC_5H_{10}, 2H), 1.32 (m, NC_5H_{10}, 1H), 0.82 (m, $PdCH_2Si$, 2H, and NC_5H_{10}, 2H), 0.14 (m, NC_5H_{10}, 1H). $^{13}C\{^1H\}$ NMR: δ 135.6 (s, Si-*i*-C_6H_5), 134.2 (s, Si-*o*-C_6H_5), 133.2 (d, $^2J_{C,P}$ = 11 Hz, P-*o*-C_6H_5), 133.1 (d, $^2J_{C,P}$ = 10 Hz, P-*o*-C_6H_5), 132.1 (s, P-*p*-C_6H_5), 131.9 (s, P-*p*-C_6H_5), 129.6 (d, $^3J_{C,P}$ = 10 Hz, P-*m*-C_6H_5), 129.4 (s, Si-*p*-C_6H_5), 129.3 (d, $^3J_{C,P}$ = 11 Hz, P-*m*-C_6H_5), 128.5 (d, $^1J_{C,P}$ = 21 Hz, P-*i*-C_6H_5), 127.9 (m, P-*i*-C_6H_5), 127.7 (s, Si-*m*-C_6H_5), 61.1 (s, $NCH_2CH_2CH_2$), 47.3 (s, NCH_2Si), 28.9 (dd, $^1J_{C,P}$ = 17 and $^2J_{C,P}$ = 8 Hz, PCH_2), 26.2 (dd, $^1J_{C,P}$ = 16 and $^2J_{C,P}$ = 4 Hz, PCH_2), 22.6 (s, $NCH_2CH_2CH_2$), 19.8 (s, $NCH_2CH_2CH_2$), 16.3 (d, $^1J_{C,P}$ = 72 Hz, $PdCH_2Si$). $^{29}Si\{^1H\}$ NMR: δ 0.88. IR: 3051 w, 2931 m, 1484 m, 1435 s, 1408 m, 1297 w, 1264 w, 1186 w, 1103 s, 1062 m, 999 w, 915 w, 828 m, 776 m, 742 s, 702 s, 659 w, 531 s, 487 m, 471 w. Anal. Calcd for $C_{45}H_{48}ClNP_2PdSi$: C, 64.75; H, 5.80; N, 1.68. Found: C, 64.43; H, 5.57; N, 1.52. Conductivity: Λ_M (Me_2CO): 30 S·cm^2·mol^{-1}.

Synthesis of [{Pd$_2$[*C*H$_2$SiPh$_2$(CH$_2$*N*C$_5$H$_{10}$)-κ^2*C,N*]$_2$Cl$_2$}-(μ-dppe)] (13). During 30 min, a solution of dppe (39.8 mg, 100 μmol) in toluene (10 mL) was added dropwise to a solution of **3** (87.3 mg, 100 μmol) in toluene (15 mL). All volatile components were removed in vacuo, and the residue was recrystallized from CH_2Cl_2/*n*-hexane at −20 °C to give 69.9 mg (55%) of **13** as a pale yellow microcrystalline solid. $^{31}P\{^1H\}$ NMR: δ 34.6 (s). ^1H NMR: δ 7.5 (m, C_6H_5, 8H), 7.2−7.0 (m, C_6H_5, 32H), 3.77 (m, NC_5H_{10}, 4H), 2.73 (s, $SiCH_2N$, 4H), 2.63 (br s, PCH_2, 4H), 2.43 (m, NC_5H_{10}, 4H), 1.65 (br m, NC_5H_{10}, 4H), 1.44 (br m, NC_5H_{10}, 8H), 0.40 (br s, $PdCH_2Si$, 4H). $^{13}C\{^1H\}$ NMR: δ 136.5 (s, Si-*i*-C_6H_5), 134.4 (s, Si-*o*-C_6H_5), 133.3 (d, $^2J_{C,P}$ = 3 Hz, P-*o*-C_6H_5), 130.7 (d, $^1J_{C,P}$ = 25 Hz, P-*i*-C_6H_5), 130.1 (s, P-*p*-C_6H_5), 128.9 (s, Si-*p*-C_6H_5), 128.3 (d, $^3J_{C,P}$ = 3 Hz, P-*m*-C_6H_5), 127.5 (s, Si-*m*-C_6H_5), 58.9 (s, $NCH_2CH_2CH_2$), 48.3 (s, NCH_2Si), 24.9 (m, PCH_2), 23.4 (s, $NCH_2CH_2CH_2$), 20.8 (s, $NCH_2CH_2CH_2$), 8.1 (s, $PdCH_2Si$). $^{29}Si\{^1H\}$ NMR: δ 1.63. IR: 3064 w, 2927 m, 2856 w, 1587 w, 1484 m, 1467 w, 1455 m, 1435 m, 1380 w, 1356 w, 1314 w, 1261 w, 1178 m, 1156 m, 1104 s, 1030 w, 999 w, 976 w, 865 w, 801 m, 766 s, 731 s, 698 s, 613 w, 520 m, 488 m, 471 w, 436 w, 410 w. Anal. Calcd for $C_{64}H_{72}Cl_2N_2P_2Pd_2Si_2$: C, 60.48; H, 5.71; N, 2.20. Found: C, 60.14; H, 5.57; N, 2.22.

Synthesis of [Pd{*C*H$_2$SiPh$_2$(CH$_2$*N*C$_5$H$_{10}$)-κ^2*C,N*}(dppe)]-BF$_4$ (14). A Schlenk flask was successively charged with **11** (56.0 mg, 67.1 μmol), thf (10 mL), and $TlBF_4$ (19.5 mg, 67.0 μmol), and the mixture was stirred for 9 h. The mixture was then filtered, and all volatile components were removed in vacuo. The residue was washed with Et_2O (3 × 3 mL) and recrystallized from thf/*n*-hexane at −20 °C to give 26.7 mg (45%) of **14** as a colorless microcrystalline solid. $^{31}P\{^1H\}$ NMR: δ 58.1 (d, $^3J_{P,P}$ = 19 Hz), 43.7 (d, $^3J_{P,P}$ = 19 Hz). ^1H NMR: δ 7.57 (m, C_6H_5, 1H), 7.5−7.1 (m, C_6H_5, 29H), 3.00 (m, NC_5H_{10}, 2H), 2.91 (s, $SiCH_2N$, 2H), 2.82 (m, NC5H_{10}, 2H), 2.27 (m, PCH_2, 4H), 1.65 (m, NC_5H_{10}, 2H), 1.33 (m, NC_5H_{10}, 1H), 0.89 (m, 2 H of $PdCH_2Si$, and 2H of NC_5H_{10}), 0.44 (m, NC_5H_{10}, 1H). $^{13}C\{^1H\}$ NMR: δ 135.7 (s, Si-*i*-C_6H_5), 134.4 (s, Si-*o*-C_6H_5), 133.5 (d, $^2J_{C,P}$ = 13 Hz, P-*o*-C_6H_5), 133.3 (d, $^2J_{C,P}$ = 12 Hz, P-*o*-C_6H_5), 132.3 (s, P-*p*-C_6H_5), 132.1 (s, P-*p*-C_6H_5), 129.8 (d, $^3J_{C,P}$ = 10 Hz, P-*m*-C_6H_5), 129.7 (s, Si-*p*-C_6H_5), 129.5 (d, $^3J_{C,P}$ = 11 Hz, P-*m*-C_6H_5), 128.6 (d, $^1J_{C,P}$ = 34 Hz, P-*i*-C_6H_5), 128.2 (d, $^3J_{C,P}$ = 36 Hz, P-*i*-C_6H_5), 128.0 (s, Si-*m*-C_6H_5), 61.4 (s, $NCH_2CH_2CH_2$), 47.1 (s, NCH_2Si), 29.0 (dd, $^1J_{C,P}$ = 36 and $^3J_{C,P}$ = 18 Hz, PCH_2), 26.7 (dd, $^1J_{C,P}$ = 31 and $^3J_{C,P}$ = 11 Hz, PCH_2), 22.8 (s, $NCH_2CH_2CH_2$), 19.7 (s, $NCH_2CH_2CH_2$), 17.0 (d, $^1J_{C,P}$ = 71 Hz, $PdCH_2Si$). $^{29}Si\{^1H\}$ NMR: δ 1.64. IR: 3063 w, 2947 w, 2857 w, 1586 w, 1484 m, 1437 s, 1407 m, 1240 w, 1187 w, 1050 s br, 997 m, 947 w, 884 w, 868 w, 820 m, 799 w, 789 w, 777 m, 753 m, 731 m, 702 s, 676 m, 654 w, 636 w, 615 w, 534 s, 484 s, 430 w. Anal. Calcd for $C_{45}H_{48}BF_4NP_2PdSi$: C, 61.00; H, 5.46; N, 1.58. Found: C, 60.86; H, 5.62; N, 1.76. Conductivity: Λ_M (Me_2CO): 105 S·cm^2·mol^{-1}.

Synthesis of [Pd{*C*H$_2$SiPh$_2$(CH$_2$*N*C$_5$H$_{10}$)-κ^2*C,N*}(S$_2$-CNEt$_2$)] (15). NaS_2CNEt_2 (40.3 mg, 250 μmol) was added to a solution of **3** (96.0 mg, 110 μmol) in CH_2Cl_2 (15 mL), and the mixture was stirred for 16 h. The mixture was then filtered, and all volatile components were removed in vacuo. The residue was recrystallized from CH_2Cl_2/*n*-hexane at −20 °C to give 96.7 mg (80%) of **15** as yellow crystals. ^1H NMR: δ 7.66 (m, C_6H_5, 4H), 7.28 (m, C_6H_5, 6H), 3.71 (q, J = 7 Hz, NCH_2, 2H), 3.69 (q, J = 7 Hz, NCH_2, 2H), 3.17 (m, NC_5H_{10}, 2H), 2.99 (s, $SiCH_2N$, 2H), 2.13 (m, NC_5H_{10}, 2H), 1.94 (m, NC_5H_{10}, 2H), 1.58 (m, NC_5H_{10}, 2H), 1.22 (m, 2H of NC_5H_{10}, and 6H of CH_3), 0.65 (s, $PdCH_2Si$, 2H). $^{13}C\{^1H\}$ NMR: δ 208.5 (s, S_2CN), 138.6 (s, Si-*i*-C_6H_5), 134.7 (s, Si-*o*-C_6H_5), 128.7 (s, Si-*p*-C_6H_5), 127.6 (s, Si-*m*-C_6H_5), 63.1 (s, $NCH_2CH_2CH_2$), 57.9 (s, NCH_2Si), 45.0 (s, NCH_2CH_3), 43.4 (s, NCH_2CH_3), 24.2 (s, $NCH_2CH_2CH_2$), 23.0 (s, $NCH_2CH_2CH_2$), 12.3 (br s, NCH_2CH_3),

Table 1. Crystallographic Data and Structure Refinement Details for Compounds 3, 4, 8, 9, 10, and 15

	3	4	8	9	10	15
cryst size [mm]	0.40 × 0.40 × 0.30	0.30 × 0.20 × 0.10	0.30 × 0.20 × 0.20	0.30 × 0.20 × 0.20	0.30 × 0.20 × 0.20	0.30 × 0.20 × 0.20
empirical formula	$C_{38}H_{48}Cl_2N_2Pd_2Si_2$	$C_{37}H_{39}ClNPPdSi$	$C_{23}H_{32}ClNPdSSi$	$C_{21}H_{30}ClNPdSSi$	$C_{31}H_{38}BF_4N_3PdSi$	$C_{24}H_{34}N_2PdS_2Si$
fw	872.72	698.64	524.53	498.49	673.96	549.18
cryst syst	monoclinic	orthorhombic	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/n$ (no. 14)	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a [Å]	9.191(2)	12.165(2)	10.205(2)	9.3408(8)	10.289(2)	9.335(2)
b [Å]	19.474(4)	15.834(3)	10.581(2)	10.4890(9)	10.788(2)	12.163(2)
c [Å]	10.737(2)	17.202(3)	22.121(4)	22.348(2)	27.852(6)	22.548(5)
α [deg]	90	90	90	90	90	90
β [deg]	104.13(3)	90	90	90	90.34(3)	99.39(3)
γ [deg]	90	90	90	90	90	90
cell volume [Å^3]	1863.6(7)	3313.5(10)	2388.6(8)	2189.5(3)	3095.5(11)	2525.8(9)
Z	4	4	4	4	4	4
ρ_{calc} [g cm^{-3}]	1.555	1.400	1.459	1.512	1.448	1.444
μ [mm^{-1}]	1.202	0.752	1.036	1.125	0.689	
no. of reflns measd	19 632	21 490	17 687	42 407	26 680	17 069
scan range [deg]	$4.44 \le 2\theta \le 54.00$	$4.84 \le 2\theta \le 54.00$	$5.32 \le 2\theta \le 50.00$	$4.28 \le 2\theta \le 50.00$	$4.22 \le 2\theta \le 52.00$	$5.54 \le 2\theta \le 54.00$
no. of unique reflns	3964	7230	4196	3858	5753	5275
no. of reflns obsd [$I \ge 2\sigma(I)$]	3545	5608	4088	3837	4337	4716
Flack param		−0.02(3)	−0.032(19)	−0.004(15)		
$R1$, w$R2$	0.0348, 0.0999	0.0435, 0.0917	0.0197, 0.0518	0.0151, 0.0401	0.0556, 0.1606	0.0337, 0.0952

−0.4 (s, Pd*C*H$_2$Si). ^{29}Si{^{1}H} NMR: δ 0.27. IR: 3061 w, 2968 w, 2928 m, 2853 w, 2809 w, 1504 s, 1461 w, 1426 m, 1379 m, 1358 m, 1303 m, 1275 m, 1212 m, 1149 m, 1109 m, 1075 w, 1036 w, 997 m, 917 m, 845 m, 765 s, 733 w, 713 m, 573 m, 531 w, 502 w, 456 w, 420 w. Anal. Calcd for $C_{24}H_{34}N_2PdS_2Si$: C, 52.49; H, 6.24; N, 5.18. Found: C, 52.25; H, 6.08; N, 5.03.

Synthesis of [Pd{*C*H$_2$SiPh$_2$(CH$_2$*N*C$_5$H$_{10}$)-κ^2*C,N*}(acac)] (16). Tl(acac) (121 mg, 400 μmol) was added to a solution of **3** (175 mg, 200 μmol) in CH_2Cl_2 (20 mL), and the mixture was stirred for 8 h. The mixture was then filtered, all volatile components were removed in vacuo, and the residue was recrystallized from CH_2Cl_2/*n*-hexane at −20 °C to give 146 mg (73%) of **16** as yellow crystals. ^{1}H NMR: δ 7.66 (m, C$_6$*H*$_5$, 4H), 7.29 (m, C$_6$*H*$_5$, 6H), 5.19 (s, COC*H*CO, 1H), 3.33 (m, NC$_5$*H*$_{10}$, 2H), 3.02 (s, SiC*H*$_2$N, 2H), 2.17 (m, NC$_5$*H*$_{10}$, 2H), 1.9 (br, NC$_5$*H*$_{10}$, 2H), 1.86 (s, C*H*$_3$, 3H), 1.83 (s, C*H*$_3$, 3H), 1.6−1.2 (br m, NC$_5$*H*$_{10}$, 4H), 1.08 (s, PdC*H*$_2$Si, 2H). ^{13}C{^{1}H} NMR: δ 187.1 (s, *C*O), 185.2 (s, *C*O), 137.7 (s, Si-*i*-C$_6$H$_5$), 134.7 (s, Si-*o*-*C*$_6$H$_5$), 128.9 (s, Si-*p*-*C*$_6$H$_5$), 127.7 (s, Si-*m*-*C*$_6$H$_5$), 99.2 (s, CO*C*HCO), 61.9 (s, N*C*H$_2$CH$_2$CH$_2$), 57.8 (s, N*C*H$_2$Si), 28.3 (s, *C*H$_3$CO), 27.2 (s, *C*H$_3$CO), 23.2 (s, NCH$_2$*C*H$_2$CH$_2$), 22.6 (s, NCH$_2$*C*H$_2$CH$_2$), −1.5 (s, Pd*C*H$_2$Si). ^{29}Si{^{1}H} NMR: δ 1.27. IR: 3065 w, 2927 w, 1591 s, 1510 s, 1402 s, 1297 w, 1260 m, 1104 m, 1020 w, 927 w, 872 m, 805 m, 780 s, 731 s, 698 s, 627 w, 605 m, 553 m, 507 m, 497 m, 435 m. Anal. Calcd for $C_{24}H_{31}NO_2PdSi$: C, 57.65; H, 6.25; N, 2.80. Found: C, 57.76; H, 6.27; N, 2.98.

X-ray Diffraction Studies of 3, 4, 8, 9, 10, and 15. Crystals were grown by slow diffusion of hexane (**3**, **4**, **15**) or Et$_2$O (**10**) into concentrated solutions of the complexes in CH_2Cl_2 at −20 °C and by slow diffusion of hexane (**8**, **9**) into concentrated solutions of the complexes in Me_2CO at −20 °C. Relevant crystallographic details are given in Table 1. Measurements were carried out on a Stoe IPDS diffractometer (**3**, **4**, **8**, **10**, **15**) and a Bruker APEX-CCD diffractometer (**9**). The structures were solved using direct and Fourier methods. Refinement by full-matrix least-squares methods (based on F_o^2, SHELXL-97); anisotropic thermal parameters for all non-H atoms in the final cycles; the H atoms were refined on a riding model in their ideal geometric positions, except for H(1A) and H(1B) at the metalated carbon centers, which were refined isotropically. SHELXS-90 and SHELXL-97 computer programs were applied.[37] X-ray crystallography data (cif) for **3** (CCDC 231970), **4** (CCDC 231969), **8** (CCDC 231968), **9** (CCDC 231965), **10** (CCDC 231967), and **15** (CCDC 231966) have been deposited with the Cambridge Crystallographic Data Center as supplementary publications.

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Supporting Information Available: Atomic positional parameters for the freely refined atoms, bond lengths and interbond angles, atomic displacement parameters, and hydrogen atom parameters; experimental data for the complex [PdPhCl(PMe$_3$)$_2$]. This material is available free of charge via the Internet at http://pubs.acs.org.

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