Bond Cleavage

DOI: 10.1002/anie.200904570

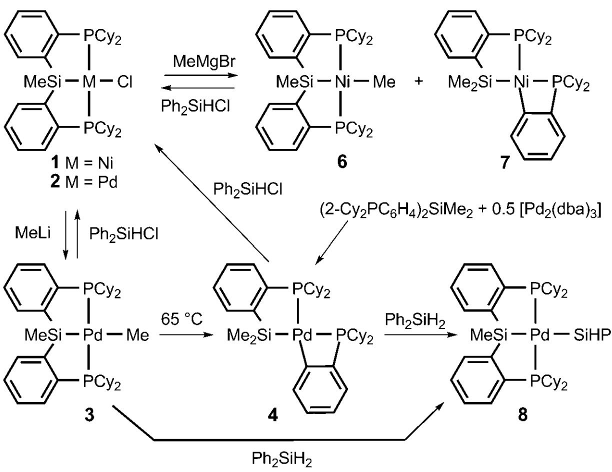
Nickel and Palladium Silyl Pincer Complexes: Unusual Structural Rearrangements that Involve Reversible Si–C(sp^3) and Si–C(sp^2) Bond Activation[**]

*Samuel J. Mitton, Robert McDonald, and Laura Turculet**

Transition-metal pincer complexes have been the subject of numerous reactivity studies that range from explorations of catalytic activity to investigations of challenging bond-activation reactions.[1] With the goal of extending the versatility of metal pincer chemistry, significant effort has been devoted to the development of new pincer-like tridentate ligands by variation of the steric and electronic properties of the donor fragments and/or the ligand backbone.[1,2] In this context, pincer ligands that feature a bis(*o*-phenylene) backbone have emerged as particularly attractive candidates for the synthesis of highly reactive early- and late-transition-metal complexes.[3–6] Such *o*-phenylene linkers provide a relatively rigid ligand architecture, and the lack of β-hydrogen atoms in the resulting complexes circumvents potential ligand degradation by β-hydride elimination. A variety of such phenylene-bridged pincer ligands have been reported, including examples where the central donor is an amido,[1a,3] phosphido,[4] carbene,[5] or silyl group.[6,7] In this regard, we have recently introduced silyl pincers of the type [κ^3-(2-$R'_2PC_6H_4)_2SiMe]^-$ ((R′–PSiP), R′ = Ph, cyclohexyl (Cy));[6a–c] we considered that the strongly electron-donating and *trans*-labilizing central Si donor may promote the formation of electron-rich and coordinatively unsaturated complexes that exhibit aggressive reactivity with σ bonds. Indeed, we have demonstrated that [(Cy–PSiP)Ir] species undergo facile arene C–H bond-activation chemistry.[6b]

We have recently begun to investigate Group 10 metal (R′-PSiP) complexes and have reported the synthesis of [(R′–PSiP)Pt^{II}] species, including examples of square-planar complexes that feature alkyl, aryl, or silyl substitution *trans* to the pincer Si donor.[6c] In expanding this chemistry to Ni and Pd, we uncovered an unusual ligand rearrangement for [(Cy–PSiPM)(alkyl)] species (M = Ni, Pd) that involves remarkably facile Si–C(sp^3) and Si–C(sp^2) bond-cleavage processes; these results are reported herein. Notably, for M = Ni, these Si–C bond-activation processes are reversible on the timescale of NMR spectroscopy in solution. Although Si–C(sp^2) bond activation is well-documented,[8] examples of unstrained Si–C(sp^3) bond cleavage within the coordination sphere of a mononuclear metal complex are extremely rare,[9,10] and are unprecedented for Ni.[11] By comparison, this ligand rearrangement was not observed in our previously reported [(R′–PSiP)Pt^{II}] chemistry.[6c]

In the pursuit of new Ni and Pd alkyl complexes, the [(Cy–PSiP)MCl] species (M = Ni, **1**; M = Pd, **2**) were treated with alkyl lithium and Grignard reagents. In the case of **2**, treatment with 1 equivalent of MeLi led to the formation of [(Cy–PSiP)PdMe] (**3**), which was isolated in 78% yield (Scheme 1).[12] The NMR spectra of isolated **3** (in [D_6]benzene) are consistent with a C_S-symmetric complex, as indicated by the presence of a single resonance in the ^{31}P NMR spectrum at $\delta = 60.5$ ppm. The ^1H NMR spectrum of **3** features a singlet resonance at $\delta = 0.72$ ppm that corresponds to the SiMe protons of the pincer ligand, as well as a triplet resonance at $\delta = 0.56$ ppm ($^3J_{HP} = 4$ Hz) that corresponds to the PdMe group. Interestingly, upon standing at room temperature, ^{31}P NMR spectroscopic analysis of a benzene solution of **3** revealed the appearance of a new C_1-symmetric species **4**, as indicated by two new resonances at $\delta = 68.3$ (d, $^2J_{P-P} = 19$ Hz) and -39.2 ppm (d, $^2J_{P-P} = 19$ Hz). Quantitative conversion to **4** was attained after heating (65 °C, 7 h), and complex **4** was isolated in 90% yield. The ^1H NMR spectrum of isolated **4** features a doublet resonance at $\delta =$



Scheme 1. Synthesis and reactivity of [(Cy–PSiP)M] complexes.

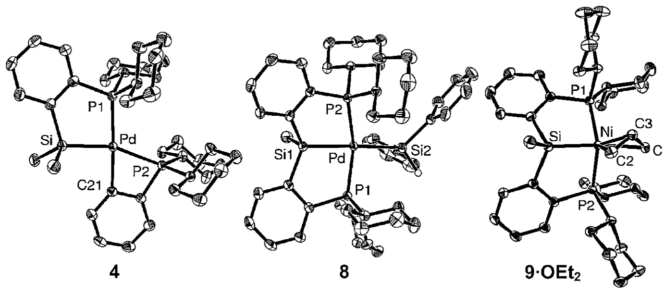
---

[*] S. J. Mitton, Prof. Dr. L. Turculet
Department of Chemistry, Dalhousie University
Halifax, Nova Scotia B3H 4J3 (Canada)
Fax: (+1) 902-494-1310
E-mail: laura.turculet@dal.ca
Dr. R. McDonald
X-Ray Crystallography Laboratory, Department of Chemistry
University of Alberta, Edmonton, Alberta T6G 2G2 (Canada)

[**] We are grateful to NSERC of Canada and Dalhousie University for their support of this work. We also thank Dr. M. Lumsden (NMR3, Dalhousie) for assistance in the acquisition of NMR data.

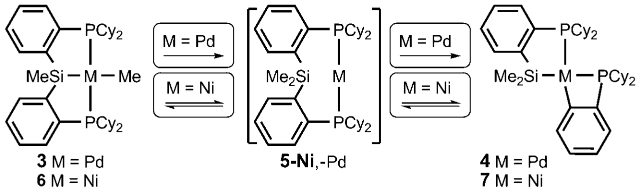
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200904570.

1.01 ppm (6H, $^4J_{H-P} = 3$ Hz) that correlates to a resonance in the ^{29}Si NMR spectrum at $\delta = 34.4$ ppm (d, $^2J_{Si-P} = 157$ Hz) in a ^{1}H–^{29}Si HMBC experiment. On the basis of these data, we proposed that **4** is a C_1-symmetric complex that features *cis*-phosphane ligands, as well as a Pd–SiMe$_2$R substituent in which the silyl group is positioned *trans* to a phosphane unit. We envisioned that such a species could arise from a rearrangement of **3** that involves net transfer of the PdMe group to Si and cleavage of a Si–C(sp^2) bond in the pincer ligand backbone to yield a four-membered Pd-C-C-P metallacycle (Scheme 1). The solid-state structure of **4** (Figure 1) was confirmed by single-crystal X-ray diffraction analysis, and is consistent with the metallacycle formulation.[12b] While alternative pathways can be envisioned, a possible mechanism for the formation of **4** could involve the intermediacy of a Pd^0 species (**5-Pd**), which undergoes Si–C(sp^2) oxidative addition (Scheme 2). Given that direct reductive elimination from **3** to afford **5-Pd** is unlikely because of the *trans*-disposed Pd–Si and Pd–Me groups, it is plausible that Si–C(sp^3) bond formation is preceded by Pd–P dissociation or a tetrahedral distortion in **3**. Support for the viability of a Pd^0 species such as **5-Pd**, which undergoes Si–C(sp^2) oxidative addition to form **4**, was obtained by the quantitative generation of **4** from the reaction of (2-Cy$_2$PC$_6$H$_4$)$_2$SiMe$_2$ with 0.5 equivalents of [Pd$_2$(dba)$_3$] (dba = dibenzylideneacetone; Scheme 1).



4 **8** **9·OEt$_2$**

Figure 1. The crystallographically determined structures of **4**, **8**, and **9·OEt$_2$**. Thermal ellipsoids are set at 50% probability; selected H atoms and the Et$_2$O solvate have been omitted for clarity. Interatomic distances [Å] for **4**: Pd–Si 2.3037(4), Pd–C21 2.087(1); **8**, Pd–Si1 2.3211(4), Pd–Si2 2.4721(4). **9·OEt$_2$**: Ni–Si 2.2344(4), Ni–C2 2.123(1), Ni–C3 2.015(1), Ni–C4 2.102(1).



Scheme 2. Rearrangement of [(Cy–PSiP)MMe] species.

Intrigued by the unusual rearrangement of **3** to **4**, we sought to prepare a NiMe derivative analogous to **3**. Treatment of **1** with 1 equivalent of MeMgBr resulted in the quantitative consumption of **1** and the clean formation of two new products, **6** and **7** (1:2 ratio, characterized by ^{31}P NMR spectroscopy; Scheme 1). Complex **6** gives rise to a single resonance in the ^{31}P NMR spectrum at $\delta = 60.0$ ppm, while complex **7** appears to have C_1 symmetry in solution and as a consequence exhibits two resonances in the ^{31}P NMR spectrum at $\delta = 68.4$ (d, 1P, $J_{P-P} = 9$ Hz) and -32.8 ppm (d, 1P, $J_{P-P} = 9$ Hz). Repeated attempts to alkylate **1** with MeMgBr under modified conditions led to reaction mixtures with an identical ratio of **6**:**7**, and heating of these reaction mixtures (up to 100 °C) did not result in increased conversion to either product. Attempts to separate **6** and **7** by precipitation or crystallization were not successful. Analysis of this product mixture by ^{1}H NMR spectroscopy indicates two SiMe resonances at $\delta = 1.02$ (d, $J_{HP} = 2$ Hz) and 0.69 ppm that correlate to resonances in the ^{29}Si NMR spectrum at $\delta = 35.0$ (d, $^2J_{SiP} = 132$ Hz) and 65.2 ppm, respectively, in a ^{1}H–^{29}Si HMBC experiment, as well as a resonance at $\delta = 0.43$ ppm (t, $^3J_{HP} = 6$ Hz) that corresponds to a terminal NiMe group. By analogy with the features of the NMR spectra recorded for **3** and **4**, compound **6** is assigned as the C_S-symmetric complex [(Cy–PSiP)NiMe], while **7** is formulated as the Ni analogue of **4** (Scheme 1). Unlike the clean formation of **3** en route to **4**, it appears that either **6** and **7** are formed independently in the case of Ni, or that by analogy with the Pd system, **6** is the product that is formed first, and in turn establishes an equilibrium with **7**.

In an effort to probe the interconversion of **6** and **7**, variable-temperature ^{1}H and ^{31}P NMR spectroscopy studies of the **6**/**7** mixture were performed ([D$_8$]toluene); no appreciable changes in the ratio of **6** to **7** were observed in the range from −80 to 90 °C. However, ^{31}P–^{31}P EXSY NMR spectra of the **6**/**7** mixture (70 °C; mixing times = 0.75 and 1.5 s) revealed chemical exchange between the magnetically non-equivalent phosphorus environments in **7** (consistent with reversible Si–C(sp^2) bond cleavage), as well as off-diagonal cross-peaks that are indicative of exchange that involves **6** and **7** (in keeping with reversible Si–C(sp^3) bond cleavage). Under similar conditions, no chemical exchange between the magnetically non-equivalent phosphorus environments in **4** was observed. The interconversion of **6** and **7** (possibly via the intermediate **5-Ni** or a related σ complex,[13] Scheme 2) was further confirmed by ^{1}H–^{1}H EXSY NMR spectroscopy experiments (70 °C; mixing times = 0.75 and 1.5 s), which revealed chemical exchange between the SiMe and NiMe environments in **6** and **7**.[14] Given the rarity of well-documented Si–C(sp^3) bond activation processes that involve first-row transition metals,[10b,15] the facile and reversible nickel-mediated Si–C(sp^3) bond cleavage reaction required for the interconversion of **6** and **7** is remarkable, especially in light of the robust nature of the Si–C(sp^3) linkage (bond dissociation energy of ca. 90 kcal mol^{-1}). The observed transformation of **3** into **4**, and the direct formation of a **6**/**7** mixture are in stark contrast to the reactivity of [(Cy–PSiP)PtMe], which does not undergo a similar rearrangement.[6c] In light of the heightened propensity of Pt for σ-bond activation (relative to Pd and Ni), it is possible that the divergent reactivity observed for these species may correlate with the barrier to accessing **5-M** (M = Ni, Pd, or Pt) from related [(Cy–PSiP)MMe] precursors.

The reactivity of **3**, **4**, and **6/7** was probed in order to gain further understanding of the possible interconversion of the terminal methyl complexes **3** and **6** with the rearrangement products **4** and **7** (Scheme 1). Treatment of isolated **3** with 1 equivalent of Ph_2SiH_2 led to the formation of [(Cy–PSiP)PdSiHPh$_2$] (**8**). The crystal structure of **8** (Figure 1) is consistent with distorted square-planar coordination geometry at Pd in which the $SiHPh_2$ ligand is coordinated *trans* to the pincer Si donor. No reaction was observed upon heating of isolated **8** (100 °C, 24 h; reaction monitored by ^{31}P NMR spectroscopy). Compound **3** also reacted with 1 equivalent of Ph_2SiHCl to form [(Cy–PSiP)PdCl] (**2**) and Ph_2SiHMe (characterized by ^{1}H and ^{31}P NMR spectroscopy). Surprisingly, treatment of **4** with 1 equivalent of Ph_2SiH_2 resulted in 50 % conversion to **8** after heating in benzene solution (96 h, 100 °C; characterized by ^{1}H, ^{31}P and ^{29}Si NMR spectroscopy). Similarly, exposure of **4** to 1 equivalent of Ph_2SiHCl led to quantitative formation of **2** and Ph_2SiHMe after heating in benzene (96 h, 100 °C; characterized by ^{1}H and ^{31}P NMR spectroscopy). Throughout the course of these reactions, no evidence of **3** was observed (by ^{31}P NMR spectroscopy). While the conversion of **3** to **2** and **8** can be viewed as proceeding with retention of connectivity within the (Cy–PSiP) ligand, the conversion of **4** to **2** and **8** requires cleavage of a Si–C(sp^3) linkage within the rearranged species **4** in order to reform the (Cy–PSiP) framework. From a mechanistic perspective, although we cannot rule out the possibility that **3** and **4** may traverse independent reaction pathways in the synthesis of **2** and **8**, it is possible that **4** transiently regenerates the terminal methyl complex **3** under the reaction conditions and/or that **3** and **4** access a common reactive intermediate such as **5-Pd** in these transformations. A similar rationale may apply in the Ni system, where the **6/7** product mixture is cleanly transformed into [(Cy–PSiP)NiCl] (**1**) with loss of Ph_2SiHMe upon exposure to 1 equivalent of Ph_2SiHCl (25 °C, 12 h); the possible intermediacy of **5-Ni** is supported by ^{31}P–^{31}P EXSY NMR spectroscopy data (see above). Monitoring of this transformation did not provide evidence for intermediates, and the ratio of **6**:**7** did not vary during the reaction (monitored by ^{31}P NMR spectroscopy).

In order to survey the scope of these unusual Si–C bond activation processes, the synthesis of Ni and Pd allyl complexes was attempted. Treatment of **1** with 1 equivalent of $(C_3H_5)MgBr$ led to the formation of [(Cy–PSiP)Ni(η^3-C_3H_5)] (**9**, 94 %).[16] Complex **9** has C_1 symmetry in solution (27 °C, [D$_6$]benzene), as evidenced by an AB pattern centered at 49.2 ppm in the ^{31}P{^{1}H} NMR spectrum; the X-ray structure of **9** is consistent with the room-temperature NMR spectroscopy data for this complex (Figure 1). No reaction was observed upon heating of isolated **9** (100 °C, 96 h; characterized by ^{31}P NMR spectroscopy). By comparison, treatment of **2** with 1 equivalent of $(C_3H_5)MgBr$ led to the formation of the C_S-symmetric complex [(Cy–PSiP)Pd(η^1-C_3H_5)] (**10**, 88 %), which features a resonance in the ^{31}P NMR spectrum at 59.1 ppm. The η^1-coordination of the allyl ligand is invoked on the basis of the allyl resonances in the ^{13}C NMR spectrum observed at $\delta = 135.2$, 87.3, and 25.3 ppm (27 °C, [D$_6$]benzene).[17] Upon heating at 70 °C for 40 minutes, 66 % conversion to **11** was observed (characterized by ^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR spectroscopy), where **11** is proposed as an analogue of **4** in which a SiMe fragment is replaced by an allyl group. Decomposition of **11** was observed with subsequent heating at this temperature. The relatively facile rearrangement observed for **10** relative to the η^3-allyl Ni complex **9** suggests that allyl η^3-coordination confers stability to the latter complex.

In summary, we have uncovered an unusual ligand rearrangement for [(Cy–PSiP)M(alkyl)] species (M = Ni, Pd). The rearrangement involves remarkably facile Si–C(sp^3) and Si–C(sp^2) bond-cleavage processes. In the case of Ni, these Si–C bond-activation processes are reversible on the timescale of NMR spectroscopy in solution. Such examples of metal-mediated cleavage of an unstrained Si–C(sp^3) bond are extremely rare, and are unprecedented for Ni. Preliminary investigations of the scope of this reaction have indicated that the rearrangement is most facile for [(Cy–PSiP)M(η^1-alkyl)] (M = Ni, Pd) species, with no reactivity of this type observed for [(Cy–PSiP)Ni(η^3-C_3H_5)] (**9**) or [(Cy–PSiP)PdSiHPh$_2$] (**8**). While the rearrangements documented herein are certainly relevant to silyl pincer systems,[6,7] ancillary ligand reactivity of this type may also play a role in the chemistry of alternative classes of pincer-like tridentate ligands that feature *o*-phenylene backbone fragments.

Received: August 16, 2009

Keywords: nickel · palladium · phosphanes · pincer complexes · Si–C activation

---

[1] a) *The Chemistry of Pincer Compounds* (Eds.: D. Morales-Morales, C. M. Jensen), Elsevier, Oxford, **2007**; b) M. E. van der Boom, D. Milstein, *Chem. Rev.* **2003**, *103*, 1759; c) M. Albrecht, G. van Koten, *Angew. Chem.* **2001**, *113*, 3866; *Angew. Chem. Int. Ed.* **2001**, *40*, 3750.

[2] For selected recent examples and reviews that highlight structural diversity, see: a) W. Leis, H. A. Mayer, W. C. Kaska, *Coord. Chem. Rev.* **2008**, *252*, 1787; b) Y. Segawa, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2009**, *131*, 9201; c) D. Pugh, A. A. Danopoulos, *Coord. Chem. Rev.* **2006**, *251*, 610; d) J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *Angew. Chem.* **2006**, *118*, 1131; *Angew. Chem. Int. Ed.* **2006**, *45*, 1113; e) W. Weng, S. Parkin, O. Ozerov, *Organometallics* **2006**, *25*, 5345.

[3] a) L.-C. Liang, *Coord. Chem. Rev.* **2006**, *250*, 1152; b) O. V. Ozerov, C. Guo, V. A. Papkov, B. M. Foxman, *J. Am. Chem. Soc.* **2004**, *126*, 4792; c) D. J. Mindiola, *Acc. Chem. Res.* **2006**, *39*, 813; d) Z. Csok, O. Vechorkin, S. B. Harkins, R. Scopelliti, X. Hu, *J. Am. Chem. Soc.* **2008**, *130*, 8156; e) W. Wei, Y. Qin, M. Loo, P. Xia, M. S. Wong, *Organometallics* **2008**, *27*, 2268.

[4] M. Mazzeo, M. Lamberti, A. Massa, A. Scettri, C. Pellecchia, J. C. Peters, *Organometallics* **2008**, *27*, 5741.

[5] T. Steinke, B. K. Shaw, H. Jong, B. O. Patrick, M. D. Fryzuk, J. C. Green, *J. Am. Chem. Soc.* **2009**, *131*, 10461.

[6] a) M. C. MacInnis, D. F. MacLean, R. J. Lundgren, R. McDonald, L. Turculet, *Organometallics* **2007**, *26*, 6522; b) D. F. MacLean, R. McDonald, M. J. Ferguson, A. J. Caddell, L. Turculet, *Chem. Commun.* **2008**, 5146; c) S. J. Mitton, R. McDonald, L. Turculet, *Organometallics* **2009**, *28*, 5122; d) J. Takaya, N. Iwasawa, *J. Am. Chem. Soc.* **2008**, *130*, 15254; e) E. E.

Korshin, G. Leitus, L. J. W. Shimon, L. Konstantinovski, D. Milstein, *Inorg. Chem.* **2008**, *47*, 7177.

[7] For related silyl pincer complexes that feature a bis(quinolyl) framework, see: P. Sangtrirutnugul, T. D. Tilley, *Organometallics* **2008**, *27*, 2223.

[8] For selected examples of Si–C(sp^2) bond cleavage by mononuclear Group 10 complexes, see: a) P. Steenwinkel, R. A. Gossage, T. Maunula, D. M. Grove, G. van Koten, *Chem. Eur. J.* **1998**, *4*, 763; b) K. Temple, A. J. Lough, J. B. Sheridan, I. Manners, *J. Chem. Soc. Dalton Trans.* **1998**, 2799; c) H. Gilges, U. Schubert, *Organometallics* **1998**, *17*, 4760; d) N. Mintcheva, Y. Nishihara, M. Tanabe, K. Hirabayashi, A. Mori, K. Osakada, *Organometallics* **2001**, *20*, 1243.

[9] For unstrained Si–C(sp^3) bond cleavage by mononuclear late-transition-metal complexes, see: a) D. E. Hendriksen, A. A. Oswald, G. B. Ansell, S. Leta, R. V. Kastrup, *Organometallics* **1989**, *8*, 1153; b) S. K. Thomson, G. B. Young, *Organometallics* **1989**, *8*, 2068; c) P. Hofmann, H. Heiss, P. Neiteler, G. Müller, J. Lachmann, *Angew. Chem.* **1990**, *102*, 935; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 880; d) P. Burger, R. G. Bergman, *J. Am. Chem. Soc.* **1993**, *115*, 10462; e) A. F. Heyduk, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2003**, *125*, 6366; f) C. M. Ong, T. J. Burchell, R. J. Puddephatt, *Organometallics* **2004**, *23*, 1493.

[10] For selected examples of Si–C(sp^3) bond cleavage in strained silacyclobutanes, see: a) D. R. Weyenberg, L. E. Nelson, *J. Org. Chem.* **1965**, *30*, 2618; b) C. S. Cundy, M. F. Lappert, J. Dubac, P. Mazerolles, *J. Chem. Soc. Dalton Trans.* **1976**, 910; c) H. Yamashita, M. Tanaka, K. Honda, *J. Am. Chem. Soc.* **1995**, *117*, 8873; d) Y. Tanaka, H. Yamashita, S. Shimada, M. Tanaka, *Organometallics* **1997**, *16*, 3246.

[11] To the best of our knowledge, reports of well-documented Si–C bond cleavage by Ni are limited to an example involving Si–C(sp) bond activation: B. L. Edelbach, R. J. Lachicotte, W. D. Jones, *Organometallics* **1999**, *18*, 4660.

[12] a) Experimental procedures and characterization data for all new compounds can be found in the Supporting Information; b) CCDC 741388 (**1**), 741390 (**4**), 741387 (**8**), and 741389 (**9·OEt$_2$**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[13] H. Fan, B. C. Fullmer, M. Pink, K. G. Caulton, *Angew. Chem.* **2008**, *120*, 9252; *Angew. Chem. Int. Ed.* **2008**, *47*, 9112.

[14] For an example of reversible Si–C(sp^3) bond cleavage in a dinuclear Ru complex, see: W. Lin, S. R. Wilson, G. S. Girolami, *Organometallics* **1994**, *13*, 2309.

[15] While nickel-catalyzed reactions of silacyclobutanes have been reported, stoichiometric reactions suggest that these transformations do not proceed by direct insertion of Ni^0 into an Si–C(sp^3) bond: K. Hirano, H. Yorimitsu, K. Oshima, *Org. Lett.* **2006**, *8*, 483.

[16] For examples of five-coordinate η^3-allyl Ni complexes, see: A. Rufińska, R. Goddard, C. Weidenthaler, M. Bühl, K.-R. Pörschke, *Organometallics* **2006**, *25*, 2308, and references therein.

[17] For examples of η^1-allyl Pd complexes, see: a) N. Solin, J. Kjellgren, K. J. Szabó, *J. Am. Chem. Soc.* **2004**, *126*, 7026; b) J. Zhang, P. Braunstein, R. Welter, *Inorg. Chem.* **2004**, *43*, 4172; c) L. Barloy, S. Ramdeehul, J. A. Osborn, C. Carlotti, F. Taulelle, A. De Cian, J. Fischer, *Eur. J. Inorg. Chem.* **2000**, 2523.