

Nickel and Palladium Silyl Pincer Complexes: Unusual Structural Rearrangements that Involve Reversible Si–C(sp³) and Si–C(sp²) Bond Activation**

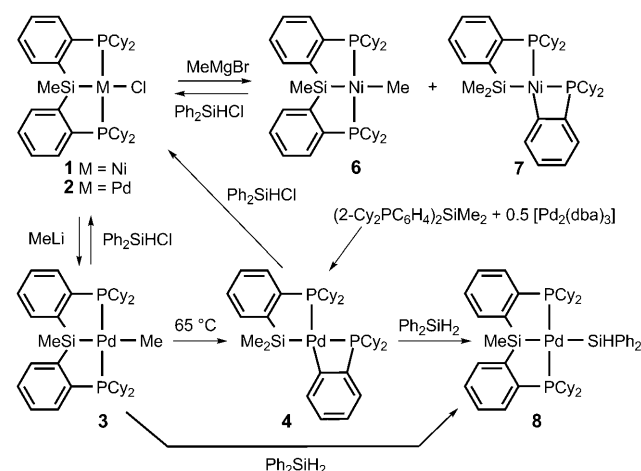
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Transition-metal pincer complexes have been the subject of numerous reactivity studies that range from explorations of catalytic activity to investigations of challenging bond-activation reactions.^[1] With the goal of extending the versatility of 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 [κ³-(2-R'₂PC₆H₄)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–PSiP)M(alkyl)] species (M = Ni, Pd) that involves remarkably facile Si–C(sp³) and Si–C(sp²) 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(sp²) bond activation is well-documented,^[8] examples of unstrained Si–C(sp³) 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



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

[D₆]benzene) are consistent with a C_s-symmetric complex, as indicated by the presence of a single resonance in the ³¹P NMR spectrum at δ = 60.5 ppm. The ¹H NMR spectrum of **3** features a singlet resonance at δ = 0.72 ppm that corresponds to the SiMe protons of the pincer ligand, as well as a triplet resonance at δ = 0.56 ppm (³J_{HP} = 4 Hz) that corresponds to the PdMe group. Interestingly, upon standing at room temperature, ³¹P NMR spectroscopic analysis of a benzene solution of **3** revealed the appearance of a new C₁-symmetric species **4**, as indicated by two new resonances at δ = 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 δ =

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1.01 ppm (6H, $^4J_{\text{H-P}} = 3$ Hz) that correlates to a resonance in the ^{29}Si NMR spectrum at $\delta = 34.4$ ppm (d, $^2J_{\text{Si-P}} = 157$ Hz) in a ^1H - ^{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-SiMe₂R 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(sp²) 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)

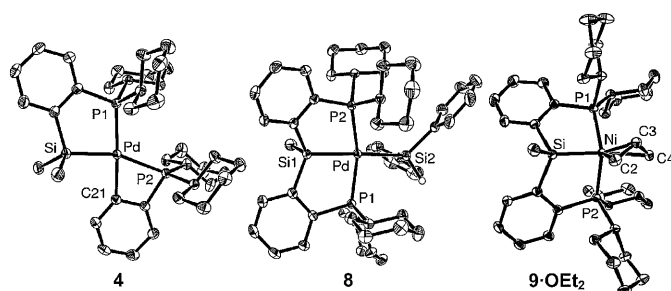
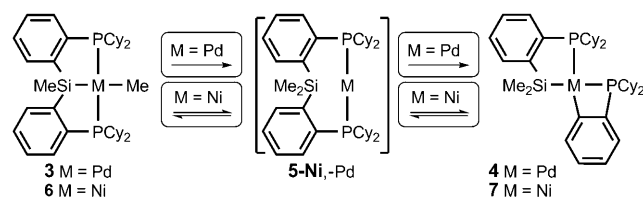


Figure 1. The crystallographically determined structures of **4**, **8**, and **9-OEt₂**. Thermal ellipsoids are set at 50% probability; selected H atoms and the Et₂O solvate have been omitted for clarity. Interatomic distances [Å] for **4**: Pd-Si 2.3037(4), Pd-C21 2.087(1); **8**: Pd-Si1 2.3211(4), Pd-Si2 2.4721(4). **9-OEt₂**: Ni-Si 2.2344(4), Ni-C2 2.123(1), Ni-C3 2.015(1), Ni-C4 2.102(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 Pd⁰ species (**5-Pd**), which undergoes Si-C(sp²) oxidative addition (Scheme 2). Given that direct reductive elimination from **3** to



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

afford **5-Pd** is unlikely because of the *trans*-disposed Pd-Si and Pd-Me groups, it is plausible that Si-C(sp³) bond formation is preceded by Pd-P dissociation or a tetrahedral distortion in **3**. Support for the viability of a Pd⁰ species such as **5-Pd**, which undergoes Si-C(sp²) oxidative addition to form **4**, was obtained by the quantitative generation of **4** from the reaction of (2-Cy₂PC₆H₄)₂SiMe₂ with 0.5 equivalents of [Pd₂(dba)₃] (dba = dibenzylideneacetone; Scheme 1).

Intrigued by the unusual rearrangement of **3** to **4**, we sought to prepare a NiMe derivative analogous to **3**. Treat-

ment 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, $J_{\text{P-P}} = 9$ Hz) and -32.8 ppm (d, 1P, $J_{\text{P-P}} = 9$ 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 ^1H NMR spectroscopy indicates two SiMe resonances at $\delta = 1.02$ (d, $J_{\text{HP}} = 2$ Hz) and 0.69 ppm that correlate to resonances in the ^{29}Si NMR spectrum at $\delta = 35.0$ (d, $^2J_{\text{SiP}} = 132$ Hz) and 65.2 ppm, respectively, in a ^1H - ^{29}Si HMBC experiment, as well as a resonance at $\delta = 0.43$ ppm (t, $^3J_{\text{HP}} = 6$ 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 ^1H and ^{31}P NMR spectroscopy studies of the **6**/**7** mixture were performed ([D₈]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(sp²) 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(sp³) 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 ^1H - ^1H 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(sp³) bond activation processes that involve first-row transition metals,^[10b,15] the facile and reversible nickel-mediated Si-C(sp³) bond cleavage reaction required for the interconversion of **6** and **7** is remarkable, especially in light of the robust nature of the Si-C(sp³) 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 Ph₂SiH₂ led to the formation of [(Cy-PSiP)PdSiHPh₂] (**8**). The crystal structure of **8** (Figure 1) is consistent with distorted square-planar coordination geometry at Pd in which the SiHPh₂ 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 ³¹P NMR spectroscopy). Compound **3** also reacted with 1 equivalent of Ph₂SiHCl to form [(Cy-PSiP)PdCl] (**2**) and Ph₂SiHMe (characterized by ¹H and ³¹P NMR spectroscopy). Surprisingly, treatment of **4** with 1 equivalent of Ph₂SiH₂ resulted in 50 % conversion to **8** after heating in benzene solution (96 h, 100 °C; characterized by ¹H, ³¹P and ²⁹Si NMR spectroscopy). Similarly, exposure of **4** to 1 equivalent of Ph₂SiHCl led to quantitative formation of **2** and Ph₂SiHMe after heating in benzene (96 h, 100 °C; characterized by ¹H and ³¹P NMR spectroscopy). Throughout the course of these reactions, no evidence of **3** was observed (by ³¹P 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(sp³) 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 Ph₂SiHMe upon exposure to 1 equivalent of Ph₂SiHCl (25 °C, 12 h); the possible intermediacy of **5-Ni** is supported by ³¹P-³¹P 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 ³¹P 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 (C₃H₅)MgBr led to the formation of [(Cy-PSiP)Ni(η³-C₃H₅)] (**9**, 94 %).^[16] Complex **9** has C₁ symmetry in solution (27 °C, [D₆]benzene), as evidenced by an AB pattern centered at 49.2 ppm in the ³¹P{¹H} 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 ³¹P NMR spectroscopy). By comparison, treatment of **2** with 1 equivalent of (C₃H₅)MgBr led to the formation of the C_s-symmetric complex [(Cy-PSiP)Pd(η¹-C₃H₅)] (**10**, 88 %), which features a resonance in the ³¹P NMR spectrum at 59.1 ppm. The η¹-coordination of the allyl ligand is invoked on the basis of the allyl resonances in the ¹³C NMR spectrum observed at δ = 135.2, 87.3, and 25.3 ppm (27 °C,

[D₆]benzene).^[17] Upon heating at 70 °C for 40 minutes, 66 % conversion to **11** was observed (characterized by ¹H, ¹³C, ³¹P, and ²⁹Si 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 η³-allyl Ni complex **9** suggests that allyl η³-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(sp³) and Si-C(sp²) 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(sp³) 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(η¹-alkyl)] (M = Ni, Pd) species, with no reactivity of this type observed for [(Cy-PSiP)Ni(η³-C₃H₅)] (**9**) or [(Cy-PSiP)PdSiHPh₂] (**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.

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