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An Unusual Example of Hypervalent Silicon: A Five-Coordinate Silyl Group Bridging Two Palladium or Nickel Centers through a Nonsymmetrical Four-Center Two-Electron Bond**

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Abstract: *Pd and Ni dimers supported by PSiP ligands in which two hypervalent five-coordinate Si atoms bridge the two metal centers are reported. Crystallographic characterization revealed a rare square-pyramidal geometry at Si and an unusual asymmetric M_2Si_2 core ($M = Pd$ or Ni). DFT calculations showed that the unusual structure of the core is also found in a model in which the phosphine and Si centers are not part of a pincer group, thus indicating that the observed geometry is not imposed by the PSiP ligand. NBO analysis showed that an asymmetric four-center two-electron (4c-2e) bond stabilizes the hypervalent Si atoms in the M_2Si_2 core.*

Since the discovery of the first hypervalent Si compounds, $[SiF_6]^{2-}$ and *trans*-$SiF_4(NH_3)_2$, in the 19th century,[1] there has been considerable research into the structure, bonding, and properties of these species.[2] These five- and six-coordinate Si compounds cannot be described in terms of two-center two-electron (2c-2e) bonds. Instead, three-center four-electron (3c-4e)[3] or three-center two-electron (3c-2e)[4] bonds are used, depending on the environment of Si.[5] As a result of their ability to stabilize electron-rich groups through hypervalency, hypervalent Si species are often postulated as crucial intermediates in organic reactions,[6] and there is continued interest in understanding the structure of this important class of compounds.

Over the last decade, pincer ligands with two phosphine donors and a central anionic Si donor (PSiP ligands) have attracted attention owing to the high *trans* influence of the Si atom and the rigidity of the pincer framework.[7] Turculet and co-workers have demonstrated that complexes supported by this ligand can undergo reversible Si−C bond cleavage,[7f] whereas Takaya and Iwasawa utilized catalysts with PSiP ligands for the carboxylation of allenes under mild conditions.[7d] Complexes supported by the PSiP ligand have not only given rise to interesting reactivity but have also led to the formation of structurally remarkable species. For example, while studying the mechanism of the carboxylation reaction, Takaya and Iwasawa were able to isolate a number of complexes with η^2-Si−H bonds; such complexes mimic the transition state for oxidative addition of a Si−H bond.[7h,j] Herein, we report the preparation of a Pd dimer supported by two PSiP ligands in which an unusual five-coordinate hypervalent silyl group bridges two Pd centers. Computational analysis revealed that the key interaction is a rare example of a four-center two-electron (4c-2e) bond. In this study, this type of bond was shown to stabilize hypervalent Si for the first time. A closely related Ni analogue of the Pd dimer, with similar bonding features, has also been synthesized and characterized by X-ray crystallography.

Recently, both our research group[7q] and Mitton and Turculet[7o] investigated the insertion of CO_2 into $[(^{Cy}PSiP)PdH]$[8] ($^{Cy}PSiP = Si(Me)(2\text{-}PCy_2\text{-}C_6H_4)_2$, in which Cy is cyclohexyl), and demonstrated that a Pd formate was rapidly generated. We were interested in exploring the same reaction with the related complex $[(^{Ph}PSiP)PdH]$ ($^{Ph}PSiP = Si(Me)(2\text{-}PPh_2\text{-}C_6H_4)_2$), which Takaya and Iwasawa proposed to be a crucial intermediate in allene carboxylation.[7d] However, treatment of $LiEt_3BH$ with $[(^{Ph}PSiP)PdCl]$ did not

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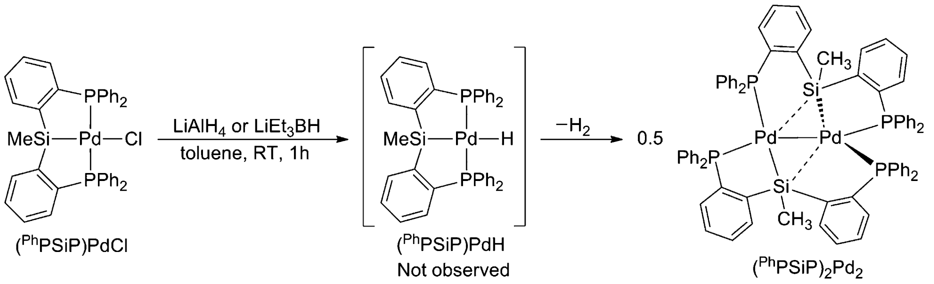
Supporting information for this article, including experimental procedures, characterization data, X-ray crystallographic information for $[(^{Ph}PSiP)_2Pd_2]$ and $[(^{Ph}PSiP)_2Ni_2]$, computational details, method calibration with different functionals, selected structural information on the optimized structures of the model compounds **1-Me** and **1-SiF$_3$**, and a list of coordinates of all optimized structures, is available on the WWW under http://dx.doi.org/10.1002/anie.201307618.



Scheme 1. Synthesis of $[(^{Ph}PSiP)_2Pd_2]$ via a proposed $[(^{Ph}PSiP)PdH]$ intermediate.

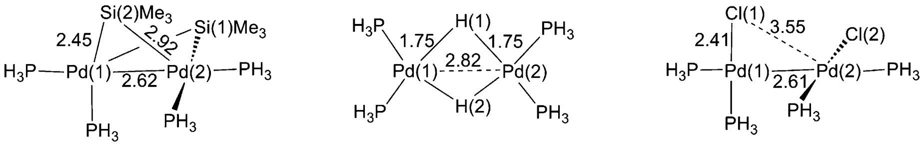
generate the expected Pd hydride. Instead, the dimer $[(^{Ph}PSiP)_2Pd_2]$ with unusual five-coordinate Si atoms bridging the two metal centers was isolated (Scheme 1). When the reaction was performed on an NMR scale, H_2 was observed as a by-product by ^1H NMR spectroscopy. However, there was no decrease in the rate of dimer formation when the reaction was performed under 1 atmosphere of H_2, thus indicating that the step involving H_2 loss is not reversible. The choice of hydride source does not appear to be crucial, as when $[(^{Ph}PSiP)PdCl]$ was treated with $LiAlH_4$ instead of $LiEt_3BH$, $[(^{Ph}PSiP)_2Pd_2]$ was observed in the ^{31}P NMR spectrum. Given that the analogous reaction between $[(^{Cy}PSiP)PdCl]$ and $LiEt_3BH$ results in the clean formation of $[(^{Cy}PSiP)PdH]$,[7q] it is probable that the formation of $[(^{Ph}PSiP)_2Pd_2]$ occurs through a transient $[(^{Ph}PSiP)PdH]$ species, although even at low temperature there is no evidence for the formation of this intermediate. Presumably, the relative lack of steric bulk in $[(^{Ph}PSiP)PdH]$ results in bimolecular dimerization, whereas the more sterically protected complex $[(^{Cy}PSiP)PdH]$ is stable.[8]

The solid-state structure of $[(^{Ph}PSiP)_2Pd_2]$ was elucidated by X-ray crystallography (Figure 1).[9] Both Si centers exhibit distorted square-pyramidal geometry, consistent with hypervalency. The degree of distortion from square pyramidal to trigonal bipyramidal was quantified by calculating the value τ.[10] On a scale of 0 to 1, where 0 denotes idealized square-pyramidal character, τ is 0.25 for Si(1) and 0.28 for Si(2). Square pyramidal is a rare geometry for hypervalent five-coordinate Si, which in general has a marked preference for trigonal-bipyramidal geometry.[2] The structure contains a puckered bicyclic core, Pd_2Si_2, in which both Pd centers form one short (ca. 2.4 Å) and one long (ca. 2.8 Å) Pd–Si bond. The geometry at each of the Pd centers is distorted square pyramidal with the more distant bridging Si atoms in the apical position. The two planes containing Pd, the two P atoms, and the closer Si center are approximately orthogonal, as shown by the dihedral angle Si(2)-Pd(1)-Pd(2)-Si(1) of 104.97(5)°. The Pd(1)–Pd(2) bond distance of 2.5860(5) Å is consistent with a Pd–Pd bond,[11] and all Si–C bond distances are similar (ca. 1.9 Å). Previously reported systems with five-coordinate silyl groups bridging two metals can be classified into two groups: 1) those that have equal M–Si bond distances, such as $[LRh(H)(\mu\text{-}Cl)(\mu\text{-}SiPh_2)(\mu\text{-}SiPh_3)Rh(H)L]$[12] and the $[Cu_5Cl_4\{Si(SiMe_3)_3\}_2]^-$ anion,[13] and 2) those that have unequal M–Si bond distances. In this latter group, complexes with $\{HSiR_2\}$ or $\{H_2SiR\}$ bridges, such as $[(R_3P)Pd(\mu\text{-}SiR'_2H)]_2$,[14] and a Ru dimer with a $\{SiR_3\}$ bridge[15] have been reported. In these complexes, a M···Si–H (or M···Si–C) 3c-2e interaction was suggested, since the closest Si–H (or Si–C) bond to the metal was longer than the other Si–H (or Si–C) bonds, and the metal center had an empty coordination site.[5b,15] Given that $[(^{Ph}PSiP)_2Pd_2]$ does not fit into either of these classes, we suggest that $[(^{Ph}PSiP)_2Pd_2]$ contains a different type of bridging Si bond to those previously reported.

We performed DFT[16] geometry optimization of $[(^{Ph}PSiP)_2Pd_2]$ to gain an understanding of the nature of the Pd–Si bonding. The short and long Pd(1)–Si(1), Pd(1)–Si(2), Pd(2)–Si(1), and Pd(2)–Si(2) bond lengths observed in the crystal structure were reproduced in the calculated structure (calc. 2.749, 2.432, 2.409, and 2.850 Å; exp. 2.7568(13), 2.3985(12), 2.3689(12), and 2.8533(13) Å, respectively). The calculated Pd–Pd bond distance was marginally longer (2.605 Å) than the observed value of 2.5860(5) Å. The square-pyramidal geometry at each Pd center and the dihedral angle Si(2)-Pd(1)-Pd(2)-Si(1) (calc. 104.5°; exp. 104.97(5)°) were also reproduced.

The lack of symmetry of the Si bridges in $[(^{Ph}PSiP)_2Pd_2]$ could be due to the chelating nature of the $^{Ph}PSiP$ ligand. To examine this hypothesis, we performed a calculation in which the chelating $^{Ph}PSiP$ ligand was replaced with PH_3 and $SiMe_3$ (model **1-Si** in Scheme 2). The optimized structure was similar to that obtained with the chelating $^{Ph}PSiP$ ligand and gave the same set of short and long Pd–Si distances. Therefore, the nonequivalence in the Pd–Si bond distances does not result from constraints imposed by the $^{Ph}PSiP$ ligand but is intrinsic to the nature of the chemical groups in the coordination sphere of each Pd atom.

The bonding in this structure is best interpreted by NBO analysis,[16g] which was performed for the full $[(^{Ph}PSiP)_2Pd_2]$ and **1-Si** systems, and for isoelectronic models in which the bridging silyl groups were replaced with bridging hydride (model **1-H**) and chloride ligands (model **1-Cl**; Scheme 2).



1-Si, θ = 94° **1-H**, θ = 180° **1-Cl**, θ = 124°

Scheme 2. Model systems used to study the Pd_2X_2 interaction, in which X = $SiMe_3$ (model **1-Si**), H (model **1-H**), and Cl (model **1-Cl**), with selected calculated distances [Å] and the XPdPdX dihedral angle (θ).

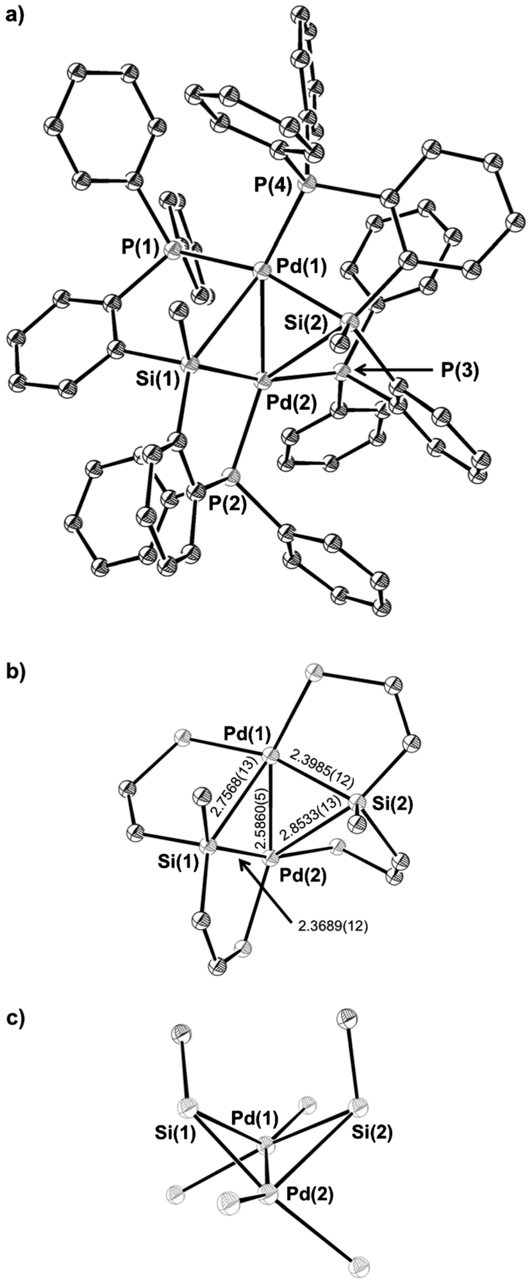


Figure 1. a) ORTEP of [(^{Ph}PSiP)$_2$Pd$_2$] with ellipsoids shown at the 30% probability level. Disorder in the phenylene backbone as well as the phenyl groups on the phosphine ligands are not displayed. Selected hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)–Pd(2) 2.5860(5), Pd(1)–P(1) 2.3639(11), Pd(1)–P(4) 2.2956(11), Pd(1)–Si(1) 2.7568(13), Pd(1)–Si(2) 2.3985(12), Pd(2)–P(2) 2.2873(12), Pd(2)–P(3) 2.3665(12), Pd(2)–Si(1) 2.3689(12), Pd(2)–Si(2) 2.8533(13); Pd(1)-Si(1)-Pd(2) 60.03(3), Pd(1)-Si(2)-Pd(2) 58.23(3), Si(1)-Pd(1)-Si(2) 88.93(4), Si(1)-Pd(2)-Si(2) 87.26(4). b) The Pd$_2$Si$_2$ core with selected bond lengths [Å]. c) Alternative view of the Pd$_2$Si$_2$ core.

Surprisingly, NBO analysis of [(^{Ph}PSiP)$_2$Pd$_2$] located five lone pairs on each Pd atom, thus indicating full occupation of the 4d orbitals of each metal by ten electrons. This electronic configuration is associated with a natural charge of essentially 0 at each Pd atom. Since the 4d orbitals of each Pd atom are fully occupied, each SiR$_3$ fragment has a single electron in a hybrid orbital available for bonding. The NBO analysis showed that the two electrons of the two silyl groups are delocalized in a four-center orbital, as shown by the natural localized molecular orbital (NLMO) formed from the two SiR$_3$ groups (35% sp^2 from each SiR$_3$ group) and the two Pd centers (11% 5s from each Pd atom; Figure 2).[17] This result is consistent with a 4c-2e bond without any diradical character. The partial population of the two Pd 5s orbitals presumably relieves some of the antibonding interaction that results from full occupation of the 4d shell,[18] and the short distance between the two Pd atoms is probably caused in part by the Pd–Pd bonding interaction associated with the 4c-2e bond. Similar results were obtained with **1-Si**.

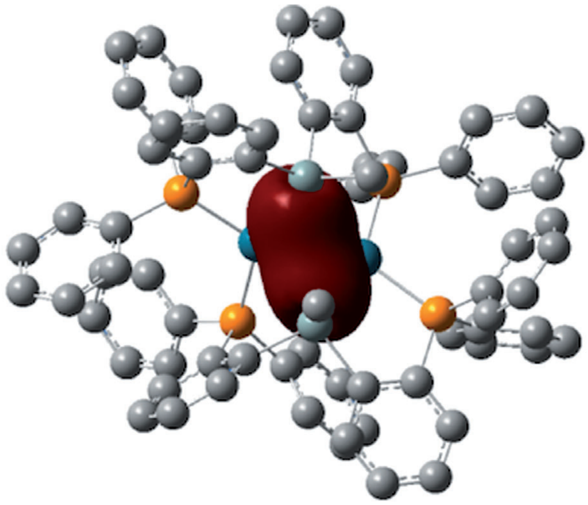


Figure 2. NLMO for the 4c-2e bond interaction in [(^{Ph}PSiP)$_2$Pd$_2$].

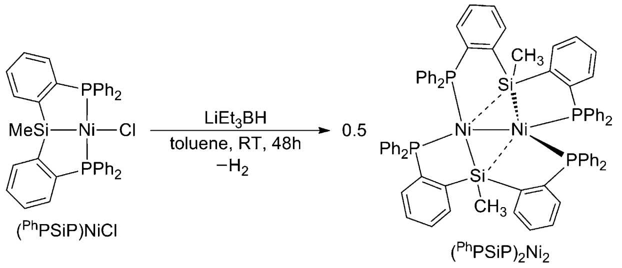
The optimized structure of the dihydride complex **1-H** (Scheme 2) shows that the two Pd centers and the two H atoms are coplanar ($\theta = 180°$), in agreement with available crystal structures.[19] Furthermore, the calculated Pd−H bond distances are equal, and the Pd−Pd bond distance (2.82 Å) is significantly longer than in **1-Si** (2.62 Å). The NBO analysis also identified five lone pairs in the d orbitals of each Pd atom, and the Pd−H bond is constructed from the H 1s orbitals (39%) and the 5s orbitals of Pd (10%). The situation is different in the dichloride complex **1-Cl** (Scheme 2). This complex is formed from two T-shaped PdClP$_2$ fragments connected through a Pd−Pd bond. The molecular planes of the two fragments make a dihedral angle θ of 124°. In this case, the NBO analysis identified four lone pairs on each Pd atom and a Pd−Pd bond constructed predominantly from the 4d orbitals on each Pd atom (95%). This change in the bonding mode is accompanied by a more positive NBO charge (+0.2) as compared to that of **1-Si** (0.0). The Pd−Cl bonds are formed as a result of electron donation from the chloride lone pairs to the 5s orbital (58%) of Pd, with a significant contribution from the 4d orbital (41%), and are equivalent to two localized two-electron bonds.

This analysis indicates that [(^{Ph}PSiP)$_2$Pd$_2$] is a remarkable example of a bonding situation that is intermediate between the symmetrically bridged dihydride and the terminally bonded mode of the chloride complex, as indicated by the nonplanarity of the complex and the different Pd−Si bond distances. It is common to consider silyl, hydride, and chloride ligands as closely related X-type ligands that are associated with a limiting oxidation state of +1 at the metal. However, this formalism has no real relationship to the actual electron density donated (or accepted) by these ligands, which is better represented by accurate calculations and analyzed on the basis of the NBO formalism.[20] In the present study, we clearly observed different Pd_2X_2 bonding modes, which depended on the exact nature of the X-type ligand. If X is electron-withdrawing and has no low-lying empty orbitals (see below), as in **1-Cl**, the 4d orbitals of each Pd atom are not fully occupied, and both 4d and 5s Pd orbitals are involved in bonding with X. These two orbitals contribute to two localized two-electron bonds in orthogonal directions.[21] An increase in the electron-donating character of X, for example, with SiR_3 (**1-Si**) or H (**1-H**), leads to Pd−X orbitals that are increasingly localized on the metal and ultimately a preference for fully occupied 4d orbitals, thus accounting for the presence of five lone pairs. In this case, only the metal 5s orbital is available for bonding with an X orbital, which formally contains a single electron. When X is spherical, such as a hydride, either planar or slightly distorted planar geometry[19] results in good overlap between X and the 5s orbitals of the Pd atoms. This arrangement generates a symmetrical bridging situation, which stabilizes the two remaining electrons. For the bridging silyl group, an unsymmetrical bonding situation is best able to stabilize the two electrons formally originating from the silyl groups (one electron per silyl group) owing to the directionality of the hybrid orbital used by the silyl group to interact with the two Pd centers. Each silyl group increases the overlap with one of the Pd centers by redirecting the hybrid orbital towards this center. As a result, a short Pd−Si bond (Pd(1)–Si(2) or Pd(2)–Si(1) in Figure 1) and a long Pd−Si bond (Pd(1)–Si(1) or Pd(2)–Si(2) in Figure 1) are observed.

In the nonsymmetrical structure of **1-Si** or $[(^{Ph}PSiP)_2Pd_2]$, an additional interaction between Pd(1) and Si(1), which the NBO analysis defines as a weak donation of a lone pair of Pd(1) into a σ* Si(1)−C bond (LP→σ*), increases the Pd–Si interaction along the long bond. The importance of this interaction, which is not reflected in the Si−C bond distances of $[(^{Ph}PSiP)_2Pd_2]$, presumably because of the large number of factors which contribute to bond lengths, becomes apparent when X groups are used that cannot be hypervalent, such as Me. Replacement of the $SiMe_3$ groups in **1-Si** with Me gives a structure **1-Me** with terminal Me groups, in analogy with the structure of **1-Cl**. In contrast, when $X = SiF_3$, a more symmetrically bridged structure appears to be preferred as compared to **1-Si**, with smaller differences between the two Pd−Si bond distances owing to increased LP→σ* donation.[22] Furthermore, in $[(^{Ph}PSiP)_2Pd_2]$, the stabilization energy gained by the LP→σ* delocalization, which favors a *trans* geometry of the Pd and C atoms at the pentacoordinated Si atom, together with steric factors associated with the close proximity of the two Si atoms (ca. 3.6 Å) in the highly constrained Pd_2Si_2 core, could account for the unusual distorted square-pyramidal geometry of Si.

Overall, the presence of the 4c-2e bond completed by two donor–acceptor interactions between the Pd atoms and the bridging Si atoms rationalizes the observed geometry in $[(^{Ph}PSiP)_2Pd_2]$. Previously, 4c-2e bonds have been invoked in the borane anion $B_6H_7^-$,[23] the scandium cluster $Sc_{24}C_{10}I_{30}$,[24] the adamantyl dication,[25] and the tetracyanoethylene anionic dimer.[26] Nevertheless, well-characterized examples of 4c-2e bonds are extremely rare, and to the best of our knowledge $[(^{Ph}PSiP)_2Pd_2]$ is the first example involving hypervalent Si.

Our analysis was carried out for Pd complexes, and it was unclear if other Group 10 metals would form similar complexes. For example, the known complex $[\{(dippe)PtH_2\}_2]$ (dippe = 1,2-bis(diisopropylphosphanyl)ethane) is a bimetallic species with a terminal hydride and a Pt−Pt bond between two T-shaped PtL_2H moieties, with L *trans* to the Pt−Pt bond, as in **1-Cl**.[27] This structure was also obtained by geometry optimization.[28] In this case, NBO analysis indicated the presence of two localized Pt−H bonds and a single Pt−Pt bond. This arrangement is consistent with the more facile oxidation of Pt relative to Pd and translates into the participation of the 5d Pt orbitals in covalent bonds. This result suggests that the formation of a platinum-based version of $[(^{Ph}PSiP)_2Pd_2]$ is unlikely. On the contrary, $[\{(dippe)NiH\}_2]$ and $[\{(Cy_2PCH_2)_2NiH\}_2]$ show almost planar geometries, similar to that of **1-H**, thus indicating a preference for a delocalized structure with Ni, as in the case of Pd.[29] Therefore, we attempted to synthesize a Ni analogue of $[(^{Ph}PSiP)_2Pd_2]$. When $[(^{Ph}PSiP)NiCl]$ was treated with $LiEt_3BH$, the dimer $[(^{Ph}PSiP)_2Ni_2]$ was isolated (Scheme 3). In an analogous fashion to the synthesis of the Pd dimer, H_2 was observed when the reaction was performed in an NMR tube. However, the reaction with Ni was significantly slower than for Pd, and an unstable intermediate that could not be characterized was observed by ^1H and ^{31}P NMR spectroscopy. The structure of $[(^{Ph}PSiP)_2Ni_2]$ as determined by X-ray crystallography was similar to that of $[(^{Ph}PSiP)_2Pd_2]$ (Figure 3).[9] The hypervalent bridging Si atoms are in a distorted square-pyramidal geometry (with τ values of 0.13 and 0.21) and form short and long bonds to Ni. As expected on the basis of the relative sizes of Ni and Pd, the Ni−Si bonds (2.3155(16), 2.3462(15), 2.4985(16), and 2.5992(15) Å) are



Scheme 3. Synthesis of $[(^{Ph}PSiP)_2Ni_2]$.

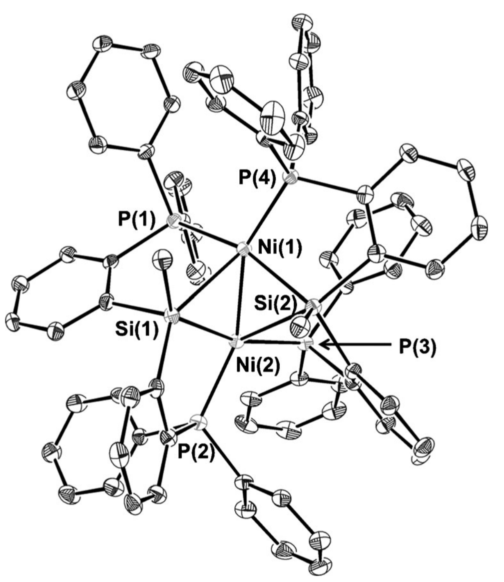


Figure 3. ORTEP of [(^{Ph}PSiP)$_2$Ni$_2$] with ellipsoids shown at the 30% probability level. Selected hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni(1)–Ni(2) 2.3057(9), Ni(1)–P(1) 2.2134(15), Ni(1)–P(4) 2.1576(14), Ni(1)–Si(1) 2.4985(16), Ni(1)–Si(2) 2.3462(15), Ni(2)–P(2) 2.1592(15), Ni(2)–P(3) 2.2116(15), Ni(2)–Si(1) 2.3155(16), Ni(2)–Si(2) 2.5992(15); Ni(1)-Si(1)-Ni(2) 57.08(4), Ni(1)-Si(2)-Ni(2) 55.29(4), Si(1)-Ni(1)-Si(2) 85.85(5), Si(1)-Ni(2)-Si(2) 84.19(5).

shorter than the Pd–Si bonds, and the Ni–Ni distance (2.3057(9) Å) is shorter than the Pd–Pd distance.

The NMR spectra of [(^{Ph}PSiP)$_2$Ni$_2$] and [(^{Ph}PSiP)$_2$Pd$_2$] are closely related. The ^{29}Si NMR spectra of both complexes displayed two resonances, at $\delta = 34.45$ and 33.25 ppm for [(^{Ph}PSiP)$_2$Pd$_2$], and at $\delta = 16.62$ and 15.81 ppm for [(^{Ph}PSiP)$_2$Ni$_2$]. These resonances are consistent with the solid-state structures. Surprisingly, only two relatively broad resonances were observed in the room-temperature ^{31}P NMR spectra of the dimers, whereas four inequivalent phosphorus atoms are present in the solid-state structures. However, at low temperature (−60 °C), four resonances were observed for [(^{Ph}PSiP)$_2$Ni$_2$], thus indicating a fluxional process that interconverts the phosphorus atoms. Given that this process must retain the inequivalence of the bridging Si atoms, it probably involves slight changes in the orientation of the phenylene backbone and the phenyl groups. It is assumed that a similar process occurs in [(^{Ph}PSiP)$_2$Pd$_2$]; however, in this case, the two phosphorus peaks were not resolved into four separate peaks even at −80 °C. The ^{13}C NMR spectra of the dimers are complicated owing to broadening of the peaks and the low solubility of the complexes in all common NMR solvents. In both cases, more than 30 peaks were observed at room temperature, which is consistent with highly asymmetric structures. The broadness of several peaks suggests fluxionality, in agreement with the ^{31}P NMR spectra.

DFT geometry optimization of [(^{Ph}PSiP)$_2$Ni$_2$] gave a structure that closely resembled the crystal structure, with Ni(1)−Si(1), Ni(1)−Si(2), Ni(2)−Si(1), and Ni(2)−Si(2) bond distances of 2.500, 2.356, 2.322, and 2.573 Å, respectively, and a Ni−Ni bond distance of 2.312 Å. NBO analysis suggested that the 4c-2e bond that is crucial for stabilizing the Pd structure is also present in the Ni species.[22]

In conclusion, we have prepared unusual Pd and Ni complexes featuring hypervalent bridging silyl groups. The main stabilization of the hypervalent Si atoms is a rare case of an unsymmetrical 4c-2e bond. We believe that this type of bonding has not been observed previously for hypervalent Si. Future studies will look to establish whether this mode of bonding is possible for metal centers other than Ni and Pd, and whether it confers unusual reactivity on the metal centers.

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$[(^{Cy}PSiP)PdH]$ with those of the related Ni complex $[(^{Cy}PSiP)NiH]$. In contrast, Mitton and Turculet proposed a structure with an η^2-silane by comparison of the NMR chemical shifts and IR stretching frequencies of $[(^{Cy}PSiP)PdH]$ with those of a related Pt complex that they had previously reported. The final product after exposure to CO_2 is unequivocally a Pd^{II} formate of the form $[(^{Cy}PSiP)Pd\{OC(O)H\}]$.

[9] CCDC 957506 ($[(^{Ph}PSiP)_2Pd_2]$) and 962272 ($[(^{Ph}PSiP)_2Ni_2]$) 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.

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