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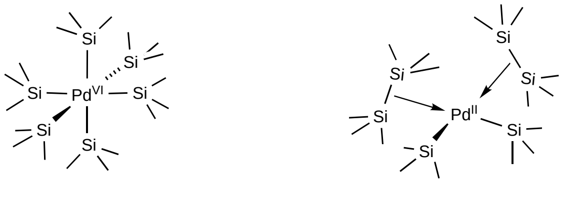
Hexakis(silyl)palladium(VI) or Palladium(II) with η^2-Disilane Ligands?**

Gabriel Aullón, Agustí Lledós, and Santiago Alvarez*

One of those earthquakes that shake from time to time the established chemical concepts has been recently provoked by the report of the thermal condensation product of three molecules of $[Pd(L)\{1,2\text{-}C_6H_4(SiH_2)_2\}]$, where L = dmpe (bis(dimethylphosphanyl)ethane) or depe (bis(diethylphosphanyl)ethane).[1] The molecular structures of the resulting trinuclear complexes, as determined by X-ray crystallography, have a central Pd atom coordinated by six silyl groups to which the highly unusual Pd^{VI} oxidation state has been assigned, as schematically shown in **1** (Scheme 1). The same authors, however, noted that an alternative interpretation of the bonding would imply a Pd^{II} oxidation state and a side-on coordination of two Si–Si single bonds (**2**; Scheme 1). In either case, the new compound would be the first one in his class, but it is appropriate to wonder whether its formulation as Pd^{VI} or Pd^{II} is a matter of taste, as happens in other transition-metal complexes with non-innocent ligands, or there are clear criteria to decide which is the right oxidation state and coordination mode.



1 **2**

Scheme 1.

Herein we present several reasons why we strongly favor the formulation of such a compound as a Pd^{II} center with two η^2-coordinated Si–Si single bonds rather than as a Pd^{VI} center with six-coordinate silyl groups:

a) The structural parameters are consistent with the square-planar Pd^{II} center formulation but not with an hexacoordinate Pd^{VI} center.

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b) Continuous symmetry measures confirm that the $PdSi_2$(centroid)$_2$ core is almost perfect square planar, whereas the $PdSi_6$ group cannot be identified as octahedral, or trigonal prismatic, or any intermediate stereochemistry.

c) Qualitative models of bonding and electronic structure predict a Pd^{VI} complex to be paramagnetic, whereas no experimental evidence of paramagnetism has been presented.

d) DFT calculations on model molecules indicate that the hexacoordinate complex has a triplet ground state and is significantly less stable than alternative structures with a Pd^{II} center and Si–Si bonds.

e) There is evidence for side-on coordination of other main-group-element single bonds.

f) The analogy between $[Pd(SiH_3)_6]$ and $[PdH_6]$ proposed by Crabtree[2] also suggests that formation of η^2-coordinated single bonds is preferred over the formation of a Pd^{VI} complex.

a) *Structural parameters*: The Si–Si distances that should be considered as nonbonding in the Pd^{VI} formulation **1**, but as bonding in the Pd^{II} form **2**, are 2.49 and 2.59 Å. Well established Si–Si bonds in Si_2Ph_6 and $Si_2(tBu)_6$ are up to 2.52[3] and 2.70 Å[4, 5] long, respectively, so it seems reasonable to consider these Si atoms to be bonded. The corresponding Si-Pd-Si angles (69.0 and 58.8°) strongly deviate from the values expected for an octahedral (90°) or a trigonal prismatic (ca. 82°) Pd coordination sphere and can be only justified by a tendency of two Si atoms to bond to each other. In contrast, if we analyze the coordination geometry by considering the centroids of the Si–Si bonds as the coordination sites, we find the following angles: centroid-Pd-centroid 93.4°, Si-Pd-Si 74.2°, centroid-Pd-Si 95.6 and 96.9°, indicative of a perfectly planar (bond angle sum of 360.1°) and nearly square $PdSi_2$(centroid)$_2$ core as expected for a tetracoordinate Pd^{II} complex.

b) *Continuous symmetry measures*: The continuous symmetry measures[6, 7] provide quantitative estimates of how much the coordination sphere of a given atom deviates from an ideal polyhedron. For the presently studied compound, we find the *distance* of the $PdSi_6$ group to the octahedron to be 13.4, which indicates that it can by no means be considered as octahedral, yet it is also far from being a trigonal prism (distance of 6.5). It has been found[8] that for structures intermediate between the octahedron and the trigonal prism the sum of the square root of these two symmetry measures must be 4.1. The value found for the present case (6.2) clearly indicates a quite anomalous $PdSi_6$ coordination polyhedron which cannot be described as an octahedron or a trigonal prism or an intermediate structure. In contrast, if we consider the centroids of the two Si–Si bonds in the Pd^{II} formulation **2**, the very small distance to the square (0.7) indicates a slightly distorted square-planar coordination sphere, consistent with the discussion on bond angles above.

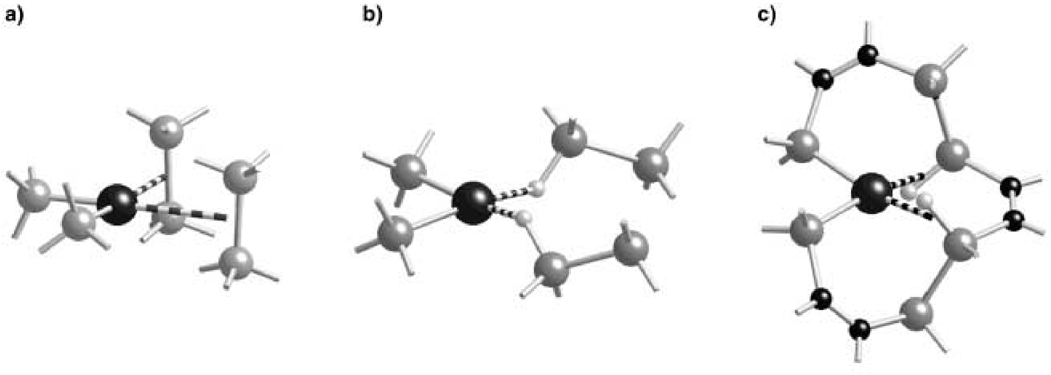


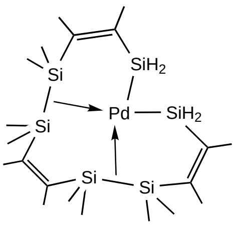
Figure 1. Calculated structures for a) $[Pd(SiH_3)_2(\eta^2\text{-}Si_2H_6)_2]$ with symmetry restrictions, b) the same model without symmetry restrictions, and c) model **3**.

c) *Spin state and magnetism*: Hexacoordinate transition-metal ions with a d^4 electron configuration may appear in either high- or low-spin states (net spins $S = 2$ and 1, respectively) in the case of first-row transition metals but only in the low-spin state for second- and third-row transition metals. In any case such d^4 configurations are paramagnetic, with the only exception of $[M(bipy)_3]$ (bipy = 2,2′-bipyridine) for M = Ti or Zr.[9] One should therefore expect the silyl–Pd^{VI} form **1** with a d^4 electronic configuration to be paramagnetic. Although the magnetic properties of these compounds have not been reported, there is no evidence of paramagnetic shifts in the published NMR spectra, clearly indicative of a diamagnetic behavior. One may argue, though, that the severe distortion of the coordination sphere from the octahedron could be responsible for a spin-paired ground state, an issue that is worth of a theoretical investigation and will be discussed below.

d) *DFT calculations*: To find out whether side-on coordination of a Si–Si bond is theoretically sound, we have carried out DFT calculations[10] on several simplified model complexes. First, we considered octahedral $[Pd(SiH_3)_6]$, which would correspond to the Pd^{VI} center **1**, and performed a geometry optimization by assuming each pair of *trans* silyl groups to be equivalent. Optimization resulted in a nearly octahedral isomer (Pd–Si bond lengths 2.491–2.497 Å and all Si–Si distances larger than 3.52 Å) more stable in its triplet than in its singlet state (by 11 $kcal\,mol^{-1}$), as expected for an hexacoordinate d^4 complex.

Next, we consider the singlet state of $[Pd(SiH_3)_2(\eta^2\text{-}Si_2H_6)_2]$ as a model of the square-planar Pd^{II} center **2**, assuming a C_2 symmetry. Such a model is indeed found to be square planar (Figure 1 a), when the centroid of the Si–Si bond is considered as the coordination site of each η^2-bonded group, and much more stable than the octahedral isomer **1** in its triplet state (by 58 $kcal\,mol^{-1}$). The interaction energy between the $Pd(SiR_3)_2$ group and two disilane units is calculated to be barely $-1.4\,kcal\,mol^{-1}$. Similar geometries were obtained for the substituted analogues $[Pd(SiH_3)_2(\eta^2\text{-}Si_2R_6)_2]$, where $R_3 = H_2Me$, HMe_2 or Me_3. An interesting result for these model compounds is that the Pd–Si distances corresponding to the η^2 groups (3.675 Å) are much longer, and the Si–Si distances

(2.329 Å) significantly shorter, than the experimental values (2.49–2.59 and 2.44–2.56 Å, respectively); however, when the Si atoms are forced to be closer to the Pd atom, the Si–Si distance is elongated. All these results reveal a quite weak bonding between the disilane molecules and the Pd^{II} center. Full relaxation of the geometry of such a compound results in the coordination of the disilane molecules through one hydrogen atom rather than through the Si–Si bond (Figure 1b, Pd–H 2.02 Å), a structure that is 9 $kcal\,mol^{-1}$ more stable than that of Figure 1a. The results for the two mononuclear models clearly indicate that the formation of Si–Si bonds combined with a Pd^{II} oxidation state is strongly favored relative to the hexakis(silyl)palladium(VI) situation.



3

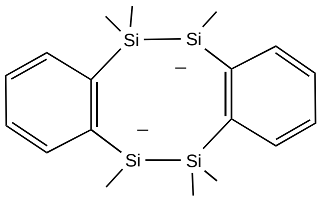
In the third model (**3**) we used the silyl ligands as they appear in the experimental structure rather than independent SiH_3 groups, replacing the benzo groups by HC=CH linkers and saturating the missing bonds from the Si centers to the peripheral Pd atoms with hydrogen atoms. The optimized structure in this case presents σ Si–H bonds coordinated to a square-planar Pd^{II} center (Figure 1c), which seems to be more stabilizing than coordination of a Si–Si bond. It is to be noted that two Si–Si bonds can be clearly identified (Si–Si 2.340 Å). The Si–H-bond coordination is probably an artifact of the model adopted, since these hydrogen atoms are replacing the peripheral Pd atoms of the experimental structure.

Finally, we have optimized the trinuclear complex with each terminal diphosphane ligand substituted by PH_3 and the benzo groups replaced by HC=CH linkers. In the absence of the artificial Si–H bonds used in the previous model, the silylated ligand of **3** is reorganized to allow for Si–Si side-on coordination to the central Pd atom. The calculated Si–Si distances (2.507 Å) as well as the corresponding Pd–Si ones (2.523 and 2.594 Å) are now in excellent agreement with the experimental data (2.538–2.554 Å and 2.420–2.565 Å, respectively). The Pd–Si bond lengths for the η^1-silyl groups (2.403 Å) are consistent with the experimental ones (2.345–2.364 Å), and even the short Pd···Pd contacts are well reproduced (2.893–2.912 Å and 2.941 Å in the experimental and calculated structures, respectively). These results clearly show that the interaction between the Pd center and the Si–Si bond is stronger than in the mononuclear model **2** because the multidentate nature of the ligand in **3** keeps them in closer contact.

That the Si–Si distance is elongated when the Pd–Si distance decreases is in agreement with a Dewar–Chatt–Duncanson-like bonding model (as applies to the η^2 coordination of the dihydrogen molecule[11]), in which each σ(Si–Si) molecular orbital donates its two electrons to the metal atom while the σ*(Si–Si) molecular orbitals of the two disilane groups accept back donation from the π-type d_{xz} and d_{yz} orbitals. The existence of two such interactions requires the Si–Si bonds to be nearly perpendicular to the $PdSi_2(centroid)_2$ coordination plane as actually found in the experimental structure and in the trinuclear model (angles of 75 and 69°, respectively).

e) *Precedents of side-on coordination of single bonds*: Although the presence of a lone pair seems a prerequisite for a particular group to act as a ligand towards a transition metal, the bonding electrons of such covalent bonds as H–H or Si–H can also act as donors. Hence, one of the aspects of transition-metal chemistry that has opened new perspectives in recent years is the study and characterization of dihydrogen complexes, in which a H_2 molecule is coordinated in an η^2 mode and is more or less elongated with respect to the free molecule.[11–13] Overwhelming evidence has accumulated in the last few years on the η^2 coordination of Si–H, Ge–H, Sn–H, and B–H bonds.[12–15] Let us quote just two remarkable examples: a C–H bond of a solvation *n*-heptane molecule found at 2.88 Å from the Fe atom in a porphyrinato complex,[16] and the structures of two complexes in which two Si–H bonds of the same molecule are coordinated to *trans* positions of a Ru atom.[17]

Even if there is no clearly established precedent for an η^2-coordinated Si–Si single bond, there is a recent report of such coordination mode for an Si=Si double bond linked to a Pt center.[18] In that compound, the Si–Si bond (2.321 Å) is clearly shorter than, but the M–Si bonds (2.432 Å) practically identical to, those in the compound studied here (2.486–2.590 Å, and 2.445–2.565 Å, respectively). It must be stressed that similar Si–Si bonds (2.69 Å) are found in a dinuclear Ni complex,[19] although the Si–Si bond was not clearly established by the authors, thus providing a fascinating example of the formation of the heterocyclic ligand **4**, the neutral octamethylated analogue of which is well known.[20] This compound should be probably considered as the first example of η^2 coordination of a Si–Si single bond to a transition metal. A related niobocene derivative also showing a dichotomy between two silyl or disilane coordinated groups has been reported more recently.[21]



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f) *Similarities between Si and H*: Crabtree[2] has suggested that the bonding situation in the compound[1] studied here should be analogous to that in $[PdH_6]$. Bayse and Hall had actually performed ab initio calculations on $[PdH_6]$ and $[PtH_6]$ and found that the former dissociates into H_2+Pd(η^2-H_2)$_2$, whereas the latter has a square-planar structure with two side-on coordinated dihydrogen molecules and two hydrides.[22] Andrews et al., on the other side, found a trigonal-planar Pd(η^2-H_2)$_3$ structure that seems to be consistent with the infrared spectra in noble-gas matrices.[23] Such studies are therefore in general agreement with the results presented here, in the sense that H–H, Si–H, and Si–Si bonds present similar coordinating abilities toward transition metals.

The assignment of a Pd^{VI} oxidation state within the $PdSi_6$ core in the recently reported compound should be disregarded according to our structural, symmetry, and theoretical analysis.[24] Nevertheless, the alternative structure is no less remarkable since it presents side-on coordination of Si–Si single bonds that are formed with a Pd complex as a template, which can now be incorporated to the gallery of other σ bonds that are known to coordinate to transition metals: H–H, C–H, Si–H, Ge–H, Sn–H, and B–H. The present study also suggests that the structure of a related dinuclear Ni complex[19] should be revisited and reinterpreted, and might be considered as the first structurally characterized example of such kind of novel coordination of Si–Si bonds.

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[10] The structures were optimized at the B3LYP level of theory implemented in Gaussian98 (Revision A.11).[10a] Effective core potentials and their associated double-ζ basis set LANL2DZ were used for Pd, P, and Si atoms, supplemented with polarization functions for Si and P, whereas a 6-31G basis set was used for H and C. The structures shown in Figure 1b–c have been charactrized as energy minima through vibrational frequencies calculations. Interaction energies were corrected for the basis set superposition error by means of the counterpoise method; a) Gaussian98 (Revision A.11), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.

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A 3D Open–Framework Indium Telluride and Its Selenide and Sulfide Analogues**

Cheng Wang, Xianhui Bu, Nanfeng Zheng, and Pingyun Feng*

There has been increasing interest in designing host–guest materials with crystalline conducting frameworks.[1] The combination of porosity and conductivity in the same material is expected to lead to unique properties suitable for electronic applications as well as molecular-sieve type applications. One application that might be envisioned to benefit from the development of host–guest chalcogenide open frameworks is in the area of thermoelectric materials, where there has been interest in developing host–guest order–disorder materials.[2] The disordered portion of the structure is expected to scatter phonons and minimize lattice thermal conductivity while the ordered crystalline framework serves to maintain high electric conductivity.[3] The recent interest in host–guest germanium–silicon clathrates reflects the application of this design strategy.[4, 5]

So far, extensive studies have been made with purely inorganic chalcogenides because of their useful optoelectronic and thermoelectric properties.[6] For example, $CuInSe_2$ is among the most efficient photovoltaic materials and Bi_2Te_3 is one of the best thermoelectric materials. In comparison, very little research has been done on the optical, electronic, and thermoelectric properties of open-framework chalcogenides. This is in part a result of the rarity of host–guest heavy-chalcogenide open frameworks. To our knowledge, no amine-templated 3D open-framework tellurides have been made prior to this work, even though some open-framework sulfides and selenides are already known.[7–11]

In the synthesis of metal-chalcogenide open-framework materials, small clusters are often found to serve as structural building units (SBUs) in extended frameworks. These clusters include supertetrahedral T2 (M_4X_{10}), T3 ($M_{10}X_{20}$), and T4 ($M_{20}X_{35}$), where M is a metal ion and X is a chalcogen anion.[12, 13] While the cluster-based structural-design approach is known to generate large pores,[12, 13] the intercluster connection is typically provided by a single atom. This situation may not represent the best configuration for electronic properties, therefore, it is highly desirable to have open-framework chalcogenides with topological features that extend beyond the cluster-based configurations.

Here we report an amine-directed, chain-based 3D telluride open framework together with its selenide and sulfide analogues. It is also demonstrated here that mixed-chalcoge-

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