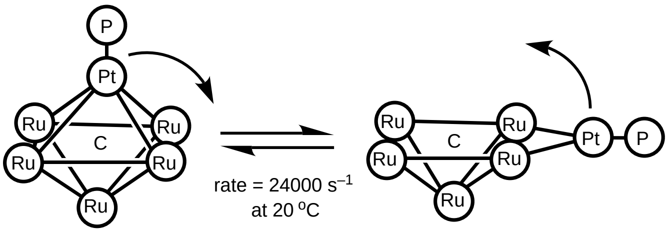

Figure 5. Interconversion of the Pt center between a fourfold and a twofold site.

The great facility of the transformation can be explained by the participation of the CO ligands that help to stabilize the open cluster through their bridging coordination to the platinum atom. Our studies of this molecular cluster model system provide an interesting and unusual new perspective of rearrangements involving the making and breaking of metal–metal bonds in polynuclear metal complexes and by analogy also of the corresponding types of transformations that occur on metal surfaces.

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[16] $[Ru_5(CO)_{15}(\mu_6\text{-}C)]$ (18.0 mg) was allowed to react with $[Pt(P\mathit{t}Bu_3)_2]$ (10.5 mg) in CH_2Cl_2 (15 mL) under a nitrogen atmosphere at room temperature for 30 min. The product was isolated by TLC to yield 13.2 mg (52%) of red crystals of $[Ru_5Pt(CO)_{15}(P\mathit{t}Bu_3)(\mu_6\text{-}C)]$ (**1**). Spectral data for **1**: IR ν_{CO} (in CH_2Cl_2): $\tilde{\nu} = 2087$ (m), 2055 (s), 2033 (s), 2028 (s), 1991 (sh), 1822 cm^{-1} (w, br); $^{31}P\{^1H\}$ NMR (−40 °C, [D$_8$]toluene, 202.5 MHz): $\delta = 118.2$ ($^1J_{Pt\text{-}P} = 5983$ Hz), $\delta = 92.7$ ppm ($^1J_{Pt\text{-}P} = 6164$ Hz); elemental analysis (%) calcd: C 25.19, H 2.02; found: C 25.28, H 1.92.
[17] Crystal data for **1** in triclinic form: $PtRu_5PO_{15}C_{28}H_{27}$, $M_r = 1334.91$, space group $P\bar{1}$, $a = 9.9510(5)$, $b = 12.1523(6)$, $c = 16.8957(8)$ Å, $\alpha = 79.797(1)$, $\beta = 87.338(1)$, $\gamma = 72.9380(10)°$, $V = 6769.1(9)$ Å^3, $Z = 2$, $T = 293$ K, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å. The final R factor $R1$(F) was 0.0384 for 7697 reflections with $I > 2\sigma(I)$. Crystal data for **1** in the monoclinic form **A**: space group $P2_1/n$, $a = 12.4684(10)$, $b = 17.9669(15)$, $c = 17.3482(14)$ Å, $\beta = 107.613(2)°$, $V = 3704.1(5)$ Å^3, $Z = 4$, $T = 190$ K, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å. The final R factor $R1(F)$ was 0.0463 for 5594 reflections with $I > 2\sigma(I)$.
[18] CCDC-181108–181110 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).
[19] Crystal data for **1** in the monoclinic form **B**: space group $P2_1/c$, $a = 14.1957(12)$, $b = 18.0213(15)$, $c = 29.027(2)$ Å, $\beta = 92.113(2)°$, $V = 3704.1(5)$ Å^3, $Z = 4$, $T = 190$ K, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å. The final R factor $R1(F)$ was 0.0379 for 14877 reflections with $I > 2\sigma(I)$.
[20] Line-shape simulations of the NMR spectra in the exchange-broadened region were preformed by using the program EXCHANGE written by R. E. D. McClung, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada.

Electronic Structure and Bonding in Hexacoordinate Silyl–Palladium Complexes[**]

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Bethany L. Kormos, Jason D. Thompson, and
Christopher J. Cramer[*]

Trimerization of $[Pd^{II}(R_2PCH_2CH_2PR_2)\{1,2\text{-}C_6H_4(SiH_2)_2\}]$ (**1**; where R = Me or Et) has been demonstrated to produce a trinuclear complex **2** where two of the Pd atoms can be readily characterized as Pd^{II} centers but the nature of the third, central Pd atom is less clear (Scheme 1, by-products not shown).[1] While this Pd atom (Pd1) is drawn in Scheme 1 as bonding directly to two Si atoms and further interacting with two Si–Si bonds, the interatomic distances from the X-ray crystal-structure data could also be interpreted to be consistent with an absence of Si–Si bonds and instead six Pd–Si bonds,[1] that is, the central metal would formally be Pd^{VI}. Both structures are without precedent in palladium coordination chemistry,[2, 3] although compounds of Pd[4–7] and Pt[8, 9] *have* been reported for inorganic compounds of the form [MF$_n$] (M = Pd, Pt; $n = 2,4,6$), where the extreme electronegativity of fluorine is exploited for the generation of higher oxidation states.[10]

To better understand the nature of the bonding in **2**, we have carried out DFT calculations on **2** and relevant model compounds. With the exception of single-point calculations using the X-ray geometries of **2a** and **2b**, all the structures were fully optimized and verified as minima by analytic frequency calculations. The functional employed was of the hybrid variety[11] and combined exact Hartree–Fock exchange with the gradient-corrected exchange and correlation functionals of Becke[12] and Lee, Yang, and Parr,[13] respec-

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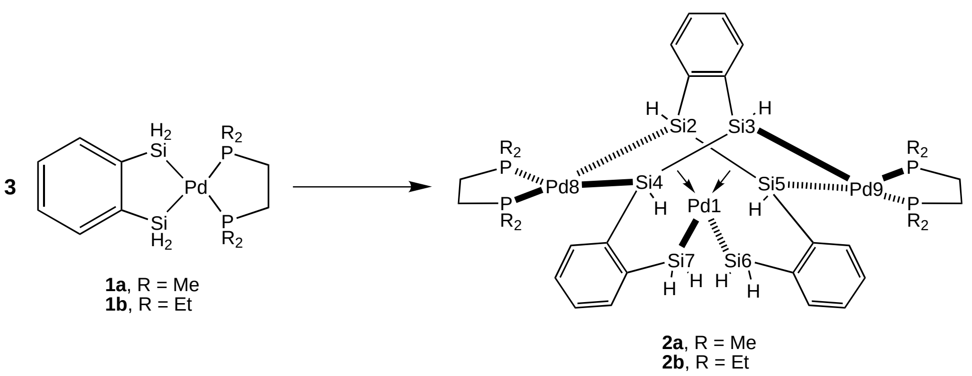

Scheme 1.

tively (B3LYP).[14] Relativistic compact effective core potentials were employed with a split-valence basis set for the Pt, Pd, P, Si, and F centers (CEP-31G);[15] d polarization functions were also included on the P, Si, and F atoms. The minimal STO-3G basis set was used for C and H atoms.[16] All the electronic states were singlets unless otherwise noted. Bond orders between atoms were computed using the method of Mayer,[17] which has been shown to be robust and relatively insensitive to basis-set size.[18–20] All calculations made use of the Gaussian 98 program suite[21] augmented with the MN-GSM package.[22]

To validate the chosen level of theory, we carried out several calculations to compare either to known experimental data or to previously published high-level calculations. In the case of $[PtF_n]$ molecules, we compute triplet ground states for $[PtF_2]$, $[PtF_4]$, and $[PtF_6]$ with Pt–F bond lengths of 1.857 Å for $[PtF_2]$, 1.871 and 1.903 Å for $[PtF_4]$ (which is Jahn–Teller distorted from square planar) and 1.882 and 1.902 Å for $[PtF_6]$ (which is Jahn–Teller distorted from octahedral). These results are in good quantitative agreement with large-basis-set B3LYP and CCSD(T) optimizations of Wesendrup and Schwerdtfeger.[23] However, both sets of calculations predict Pt–F bonds that are somewhat too long in $[PtF_6]$, the only experimentally characterized platinum fluoride compound; gas-phase electron diffraction results provide an average Pt–F length of 1.853 Å.[9] The error may be a result of large relativistic effects that are not fully accounted for in the computed values.

In the case of the more relevant palladium fluorides, experimental structures have been reported from $[PdF_2]$[4] and $[PdF_4]$[5] powder studies, but the instability of $[PdF_6]$ has not yet permitted any structural analysis.[6] These species and other fluorinated Pd^{II} and Pd^{IV} compounds have network-solid characteristics which can significantly affect Pd–F bond lengths in the crystal—in an analysis of 32 such palladium fluorides observed lengths vary from 1.86 to 2.25 Å.[7] In the gas phase, we compute $[PdF_2]$ to have a triplet ground state with a Pd–F bond of 1.902 Å, well within the experimental range although shorter than the only prior calculation of 1.94 Å at the less complete Hartree–Fock theoretical level.[24] We also predict $[PdF_4]$ to have a triplet ground state and a square planar geometry with a Pd–F bond of 1.874 Å, again within the experimental range, although at the low end.

Finally, we compared the optimized structure of **2a** to its X-ray crystal-structure geometry. The theoretical structure has C_2 symmetry, while the crystal structure is slightly distorted from symmetric. The mean difference over all 36 Pd–Pd, Pd–Si, and Si–Si interatomic distances in the two structures is 0.078 Å, while the heavy-atom root-mean-square displacement is 0.441 Å. These differences are reasonably small and entirely consistent with what might be expected from crystal packing effects; in particular, the theoretical interatomic separations are always slightly larger than those found in the crystal structure (see below). Such agreement in geometrical details bodes well for the accuracy of the molecular electronic structure. Insofar as analyses carried out for the two alternative geometries of **2a** as well as the crystal geometry of **2b** provided quantitatively similar bond orders, Kohn–Sham orbitals, etc., we restrict further discussion to the symmetric theoretical structure of **2a** so as to simplify data presentation.

To establish a calibrating scale for our analysis, we first computed optimized geometries and Mayer bond orders for the singlet ground states of $[Pd(SiH_3)_2]$ (**3**), $[Pd(SiH_3)_4]$ (**4**), and $[Pd(SiH_3)_6]$ (**5**; Figure 1). Bonding in **3** is entirely consistent with a formal Pd^{II} oxidation state: the total Pd–Si bond order is 2.00, and the Pd–Si bond lengths are 2.320 Å. Nevertheless, there is a small amount of direct Si–Si bonding, with an interatomic separation of 3.063 Å and a bond order of 0.20. This situation is very similar to that found for monomer **1a**, although in that case the ligating phosphorus atoms additionally make dative bonds to the Pd center—these bonds have bond order 0.71—and this lengthens and very slightly reduces the bond order for the Pd–Si bonds.

In **4**, the situation is rather different. The two pairs of symmetrically related Pd–Si bonds have lengths in excess of 2.45 Å, and two Si–Si distances of 2.720 Å are found. The four Pd–Si bond orders sum to only 2.96, while the interacting Si–Si fragments are predicted to have bond orders of 0.43. Thus, even with only 4 SiH_3 ligands, a tendency toward multicenter delocalized bonding is observed that would tend to argue for a formal oxidation state of less than the total number of ligands.[2] Analysis of **5**, which is found as a local minimum on starting from an octahedral initial geometry, suggests that further oxidation of the Pd center cannot be accomplished by SiH_3 as a ligand. Instead, a disilane molecule (Si–Si bond order of 0.97) is effectively ejected, and a weak complex resembling **4**·disilane is formed. In this case, the disilane molecule breaks the molecular symmetry so that one pair of SiH_3 ligands is nearly as strongly bound as in **3** while the other pair is *less* strongly bound than in **4**, but not completely ejected as disilane (the Si–Si bond order is 0.57). The total Pd–Si bond order in **5** is 3.11. The coordination geometry, where the coordinating fragments are two SiH_3

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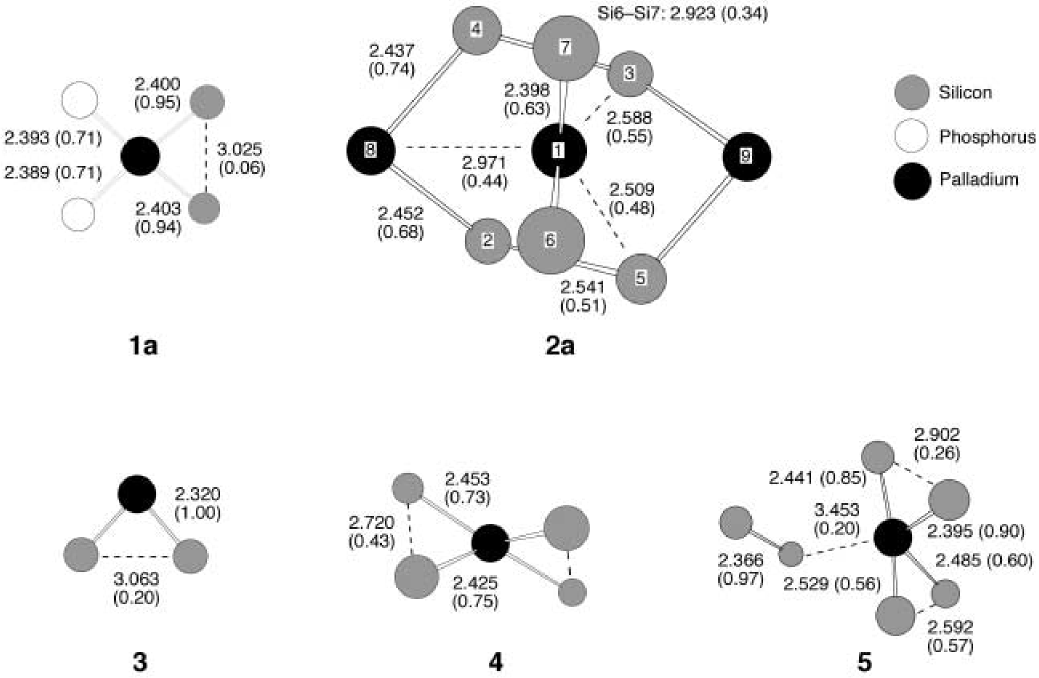

Figure 1. B3LYP optimized bond lengths [Å] and bond orders (in parentheses) for Pd–Pd, Pd–P, Pd–Si, and Si–Si bonds in compounds **1**–**5**. Other atoms have been removed for clarity. Atom numbering for **2a** is consistent with Scheme 1.

groups, one Si–Si σ bond, and one hydrogen atom of disilane, is approximately square planar, which is consistent with a Pd^{II} oxidation state.[25]

Within this context, the bonding in **2a** is readily rationalized. Just as in **5**, there are two Si atoms that are most strongly bound (Si6 and Si7, with Pd–Si bond orders of 0.63) but the overall symmetry of the complete molecule reduces the difference between "bonding" and "non-bonding" interactions. Thus, the remaining Pd–Si bond orders are 0.48 and 0.55, with a total Pd–Si bond order of 3.32. Computed Si–Si bond orders are consistent with these trends: weak between Si6 and Si7 (0.34) and stronger between the other two relevant pairs (0.51). Interestingly, in the trinuclear complex, a bond order of 0.44 is found between the central Pd and each of the other Pd atoms. This suggests some Pd cluster aspects in the overall bonding, and is consistent with Pd–Si bond orders of 0.68 and 0.74 between these outer Pd atoms and the Si atoms to which they are formally bonded, but less strongly so than computed for monomer **1**. All the bond lengths follow the trends expected based on the above analysis of bond orders.

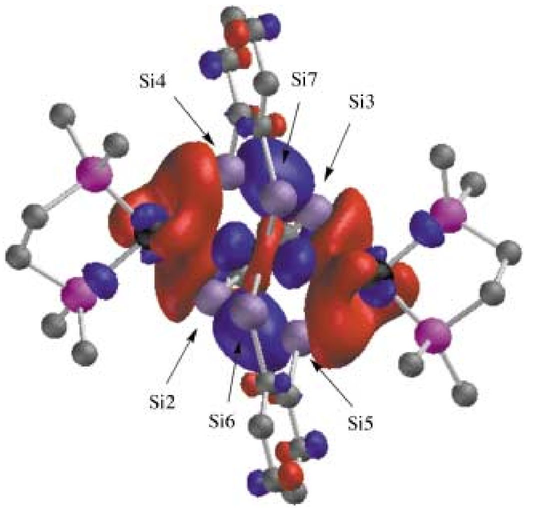

Figure 2. B3LYP HOMO for **2a**. Atom numbering is consistent with Scheme 1 and Figure 1. Hydrogen atoms have been removed for clarity.

Support for the coordination shown in Scheme 1, as opposed to hexavalent Pd^{VI}, is further offered by the highest occupied molecular orbital (HOMO) for **2a** (Figure 2). The HOMO is dominated by σ bonding between Si3 and Si4 and symmetrically related Si2 and Si5. These σ bonds hybridize in an interesting way with d_{xy} orbitals on the outer Pd atoms and the d_{z^2} orbital of the central Pd atom, but the contribution from the metal orbitals, particularly the central one, is relatively minor.

Thus, the bonding in **2a** is rather similar to that found in **5**, except that structural constraints in the former seem to reduce the total variation over all the Pd–Si bond orders compared to the latter. In that sense, the greater degree of delocalized, multicenter bonding in **2a** resembles that found in **4**. That so many different Pd–Si bond orders are so readily accommodated in **1**–**5** suggests that the ligand environment about a $PdSi_6$ fragment may be quite fluxional, and this is consistent with our interpretation above that crystal packing forces are sufficient to explain the small observed deviation of the C_2-symmetric theoretical structure from the X-ray crystal structure.

As Crabtree has pointed out,[2, 3] in delocalized bonding situations such as that computed for **2** there is no simple way to assign a metal oxidation state. However, it seems clear that assigning the central metal to be Pd^{VI} is *not* warranted for **2**, unless such an assignment is permitted to encompass the ambiguity of multicenter, delocalized bonding, to which it must be noted that silyl groups appear to be particularly apt, with no obvious preference for integer bond orders. As a theoretical model, Mayer bond orders computed from DFT density matrices clearly provide a useful tool for quantifying this phenomenon.

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

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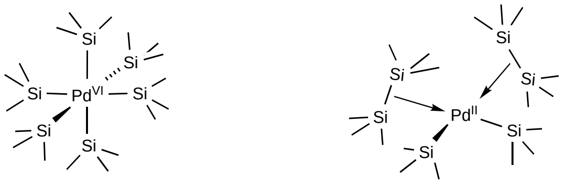
One of those earthquakes that shake from time to time the established chemical concepts has been recently provoked by the report of the thermal condensation product of three molecules of $[Pd(L)\{1,2\text{-}C_6H_4(SiH_2)_2\}]$, where L = dmpe (bis(dimethylphosphanyl)ethane) or depe (bis(diethylphosphanyl)ethane).[1] 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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