## COMMUNICATION

Semi-bridging σ-Silyls as *Z*-type Ligands

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The reactions of SiHPh(NCH₂PPh₂)₂C₆H₄-1,2 with a range of zerovalent group 10 reagents afford the homoleptic bimetallic complexes [M₂{μ-κ³-*Si,P,P'*-SiPh(CH₂PPh₂)₂C₆H₄}₂] (M = Ni, Pd, Pt) in which the M–M bond is unsymmetrically bridged by two σ-silyl groups. The assymmetry of the M₂Si₂ core increases from Ni through Pd to Pt and is consistent with a bonding description in which one metal acts as an electron pair donor to a trigonal bipyramidal '*Z*-type' silicon centre, reminiscent of semi-bridging coordination by CO, carbynes and boryl ligands.

Heavier p-block elements distinguish themselves from first row elements through hyper-valency, *i.e.*, valence shell expansion beyond that dictated by the octet rule, thereby allowing access to higher coordination numbers. Thus the chemistry of silicon(IV), especially when bearing electronegative substituents, often involves the formation of Lewis acid-base interactions in five and six co-ordinate geometries.[1] In recent times, the possibility that transition metals might serve as Lewis bases to main group Lewis acids (so-called *Z*-type ligands[2]) has emerged. For dative (polar covalent) bonding between a transition metal and 4-coordinate boron,[3,4] aluminium[5] or gallium[6] and 3-coordinate beryllium,[7] hypervalency need not be invoked. Within group 14, dative bonding between a metal and silicon or tin,[8] evokes hyper-valency and has previously been demonstrated by Wagler with the isolation of methimazolyl bridged lantern complexes of the form [MA(μ-mt)₄XY] (A = Si, Sn; M = Ni, Pd, Pt; X,Y = F, Cl, Br, I; mt = methimazolyl) and [PdSn(μ-mt)₂Cl₂(PPh₃)].[9]

Since Stone and Spencer's discovery of μ-silyl-bridged diplatinum complexes (Scheme 1a),[10] numerous related examples have appeared, however the vast majority involve supplementary 3-centre, 2-electron Si–H–metal interactions.[11] Only compara-tively recently have the first groups 10 examples of μ-silyl complexes, [M₂{μ-SiMe(C₆H₄PPh₂)₂}₂] (M = Ni, Pd, Scheme 2) been described that are devoid of such interactions, for which the silicon coordination could be explained by an unsymmetrical 4-centre, 2-electron Si-M-M-Si bond.[12] Computational interrogation of the model complexes [M₂(μ-SiMe₃)₂(PH₃)₄] (M = Ni, Pd) reproduced unsymmetrical butterfly

M₂Si₂ geometries similar to those found experimentally with alternating long and short M–Si bond lengths. Notably, the authors concluded that this type of bonding situation would be unlikely for the heavier platinum analogue, which indeed remains unknown. We report herein, a complete triad of group 10 bimetallic μ-silyl complexes in which not only is an unsymmetrical folded parallelogram geometry adopted, but the asymmetry becomes *increasingly pronounced* on descending the group to platinum.
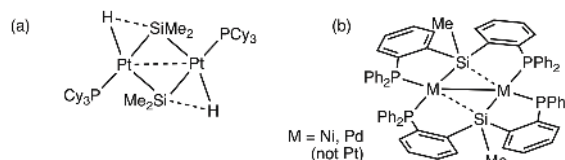

Scheme 1. Germane μ-silyl Complexes from (a) Stone[10] and (b) Hazari.[12]

Pincer ligands[13] favour a *meridional* co-ordination of three donor groups, encouraged by inclusion of trigonal donors in the equatorial site, *e.g.*, *N*-heterocyclic carbene, σ-aryl or pyridine groups. The inclusion of *tetrahedral* silyl donors in this position, however, somewhat discourages the *mer* geometry,[13d] *e.g.*, Tilley has shown that a square-planar platinum(II) bis(8-quinolyl)silyl pincer complex [PtCl{SiR(C₉H₇N)₂}] readily activates dihydrogen so as to adopt a more relaxed octahedral geometry in the complex *fac*-[PtH₂Cl{SiR(C₉H₇N)₂}].[14] We have previously described the synthesis and reactions of silyl pincer pro-ligands HSiR{(NCH₂PPh₂)₂C₆H₄} (R = Cl **1**, Me **2**, Ph **3**) that readily install a PSiP-LXL[2a] pincer system which favours the *meridional* geometry due to the rigidly planar 2,1,3-benzosiladiazol-2-yl backbone (Scheme 2).[15] Further to our own studies on d⁶-octahedral ruthenium(II) and rhodium(III) centres, related ligands have also been installed on rhodium(I),[16a] iron(II) and cobalt(II) centres.[16b,c] We have now turned our attention to group 10 metals. The complex [PdBr(C₆H₅)(PPh₃)₂] was initially chosen so as to include a σ-phenyl co-ligand that might serve as
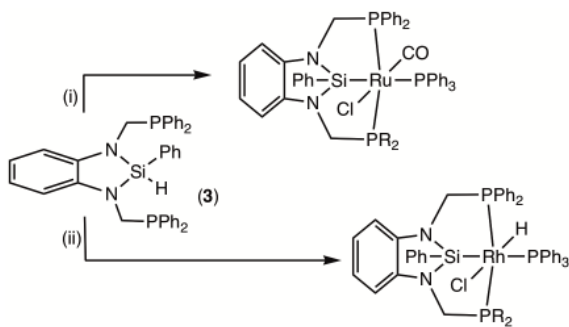
Scheme 2. Introduction of PSiP pincer ligands to Ru(II) and Rh(III) *via* Si–H activation. (i) [RuCl(Ph)(CO)(PPh₃)₂], (ii) [RhCl(PPh₃)₃].[15]

a hydrogen acceptor to thereby return the palladium to its divalent state following Si–H activation (*cf.* Scheme 2). This however resulted in palladium mediated hydrolysis of **3** and similar outcomes were encountered with [MCl₂(cod)] (cod = 1,5-cyclo-octadiene, M = Pd, Pt). Accompanying this hydrolysis was a minor trace product identified as [Pd₂{μ-SiPh(NCH₂PPh₂)₂C₆H₄}₂] (**4**, Scheme 3) and traces of **4** were also observed when either [Pd₂(μ-Cl)₂(MeOcoe)₂] (MeOcoe = 5-methoxy-cyclo-octen-6-yl) or [PdCl₂(PPh₃)₂] and Et₃N were employed. A near quantitative direct synthesis of **4** was, however, achieved *via* the reaction of **3** with [Pd₂(dba)₃] (dba = dibenzylideneacetone) in which dba is partially hydrogenated to *E*-1,5-diphenylpent-1-en-3-one (Scheme 3). The $^{31}P\{^{1}H\}$ NMR spectrum for **4** comprised two apparent triplet resonances (**AA'BB'**: δ_P = 44.9, 25.1; $J_{AB} \approx J_{AB'}$ = 10.5 Hz). The complex **4** could also be prepared from **3** and [Pd(PPh₃)₄], whilst the corresponding nickel and platinum complexes [M₂{μ-SiPh(NCH₂PPh₂)₂C₆H₄}₂] (M = Ni **5**, Pt **6**, Figure 1) were prepared from **3** and [Ni(cod)₂], [Pt(η²-C₂H₄)(PPh₃)₂] or [Pt(nbe)₃] (nbe = norbornene) (Scheme 3).
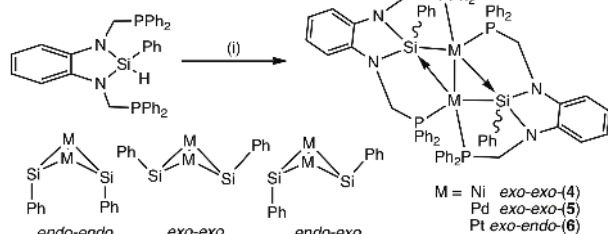
Scheme 3. Synthesis of bimetallic μ-silyl complexes *via* Si–H activation. (i) [Ni(cod)₂], [Pd(PPh₃)₄], [Pt(η-C₂H₄)(PPh₃)₂], [Pd₂(dba)₃] or [Pt(nbe)₃]; cod = 1,5-cyclo-octadiene, dba = dibenzylidene acetone, nbe = norbornene.

Spectroscopic data for **5** and **6** are generally comparable to those for **4**, though for **6** two silicon environments were observed (δ_{Si} = 58.4, 60.5, *vide infra*), whilst for **4** (δ_{Si} = 58.4) and **5** (δ_{Si} = 56.0) single multiplet resonances indicated a single silicon environment. For mononuclear complexes of the siladiazolyl pincer[15] the ^{29}Si resonances are typically found in the region 85-115 ppm, however increased shielding by two metals in **4-6** shifts these upfield to 50-60 ppm. However, it should be noted that the $^{31}P\{^{1}H\}$ NMR data for the three complexes when considered together have curiously different appearances. As noted, **4** presents what appears to be two triplet resonances while the pattern for **5** (two double-doublets)

conforms to expectation for an **AA'BB'** system. For **6**, however, to simulate the observed spectrum a large value of $^{3}J_{AA'}$ is required while $^{2}J_{AB}$, $^{3}J_{AB'}$ and $^{2}J_{BB'}$ are essentially zero. We are unable to account for this unusual behaviour but note that **6** adopts the *exo-endo* conformation (*cf. exo-exo*-**4/5**) which may contribute a dihedral angular dependence on the magnitude of ^{3}J coupling. The slower rates of intramolecular fluxional processes upon descending a group may also play a role.

Each of **4**, **5** and **6** were structurally characterized (Figure 1 and ESI). Superficially, the three complexes appear similar however closer scrutiny reveals notable differences. Complexes **4** and **5** adopt geometries in which the two Si–Ph groups are on the same side (*syn* = *exo,exo*) of the M₂Si₂ quadrilateral. For **6** the two groups have an *anti* (= *endo, exo*) disposition with distinct chemical environments, thereby accounting for the observation of two silicon environments in solution (^{29}Si NMR) for **6** but only one for **4** and **5**. In each case the M₂Si₂ quadrilateral is folded along the metal-metal vector and this is most pronounced for platinum with an interplanar hinge angle of 137.2°. Most intriguing, however, is the clear alternation of M–Si bond lengths around each M₂Si₂ ring. For **5** this is modest (25 pm) but increases for **4** (60 pm) and is most apparent for **6** (300 pm). In simple valence bond terms, the unsymmetrical bridging might be described as involving an essentially conventional short σ-bond to one platinum, supported by a longer dative bond from the second platinum. This perspective draws on analogies with *semi-bridging* carbonyl,[17] carbyne[18] and σ-boryl[19] ligands (Scheme 4), whereby electroneutrality is served by transfer of electron density from an electron-rich metal centre to an acceptor orbital on an adjacent ligand. The parallel with semi-bridging σ-boryl ligands is especially apt given that Peters has shown that [Ni(cod)₂] reacts with HB(NCH₂PPh₂)₂C₆H₄ to provide [Ni₂{μ-B(NCH₂PPh₂)₂C₆H₄}₂] (**7**) the topology of which is remarkably similar to **5**, but which has a highly folded (112.9°) B₂Ni₂ core with unsymmetrical semi-bridging boryl coordination across a Ni–Ni bond (2.2421(9) Å) that is considerably shorter (0.36 Å) than found in **7** (2.6019(7) Å).[20]

Whilst simple canonical forms help to conceptualise, they obscure the complexities of multi-centre multi-electron bonding and given the results of Nova and Hazari, we have computationally interrogated the bonding of **4**, **5** and **6** at the MO6 level of theory. For consistency, we have also considered the bonding of **6** at the MO6L level of theory employed previously to describe [Pd₂{μ-SiMe(C₆H₄PPh₂)₂}₂],[12] which accounts well for dispersion effects. The experimentally determined geometries for **4, 5** and **6** (Table 1) were adequately reproduced at the MO6L level of theory. The significantly increased folding on going from **4** (166.8°) to **5** (160.2°) to **6** (137.2°) is also reproduced computationally, though not as pronounced. Contrary to previous contention, **6** displays the most pronounced asymmetry and the bonding will be discussed in detail.

Amongst the manifold of orbital interactions supporting the Pt₂Si₂ core (Figure 2), the HOMO-2 is noteworthy in most closely representing a conventional Pt–Pt bond, which nevertheless comprises considerable contribution from two of the
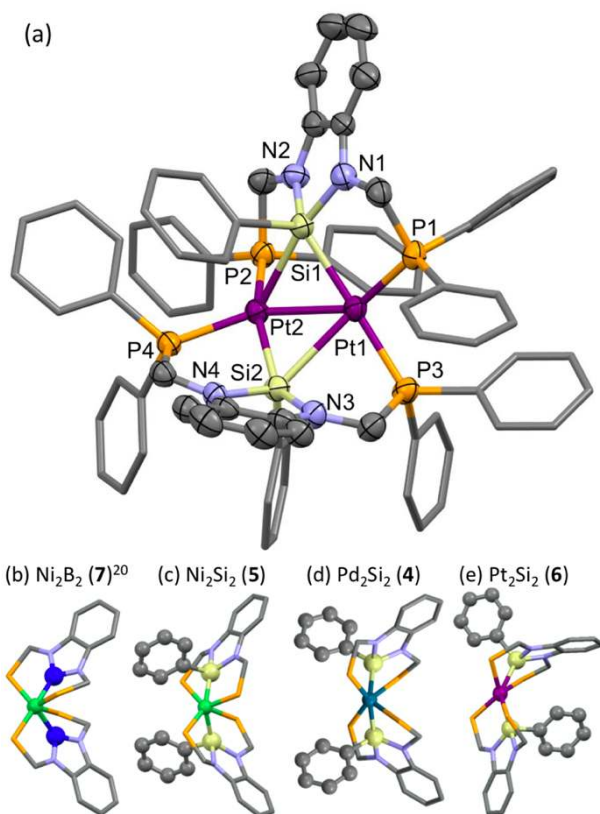
Figure 1. (a) Molecular structure of **6** in a crystal of **6·(C₆H₆)₂**. Displacement ellipsoids are drawn at the 60% level, phenyl groups are simplified and all hydrogen atoms are omitted for clarity. For geometric data see Table 1. (b)-(e) Views along the metal-metal vector of compounds **4**-**6** to illustrate folding of inner core

Table 1. Geometrical Features of the complexes **4**, **5** and **6**.

M-M	Ni–Ni (5)	Pd–Pd (4)	Pt–Pt (6)	Pt–Pt Calcd.
M–M (Å)	2.6019(7)	2.788(1)	2.7200(3)	2.78
M–Si (Å)	2.3212(9)	2.414(3)	2.380(2)	2.45
	2.294(1)	2.476(3)	2.641(3)	2.66
	2.3131(9)	2.410(3)	2.378(2)	2.44
	2.290(1)	2.470(2)	2.715(1)	2.61
M–Si–M (°)	68.77(3)	69.51(7)	65.36(4)	66.64
	68.69(3)	69.68(7)	64.17(4)	65.83
Si–M–Si	109.03(4)	109.35(9)	102.67(5)	104.65
	108.62(4)	109.29(9)	104.96(5)	109.55
Fold angle (°)	160.2	166.8	137.2	139.43
Conformation	exo-exo	exo-exo	endo-exo	endo-exo

semi-bridging character (Cb = η⁵-C₂B₉H₉Me₂).[17-19]

phosphorus centres and is thus a 4-centre, 2-electron P1–Pt1–Pt2–P2 bond *cf.* the Si–Pd–Pd′–Si′ bond described by Nova and Hazari. The HOMO-5/6 pair best reflect the canonical description of a polar-covalent dative bond from platinum to silicon. NBO analysis shows that each Pt-centre has three different component interactions with both the Si atoms. This is also supported by NBO second order Perturbation Theory analysis (donor-acceptor) from which it follows that there is a significant σ-back donation from one Pt centre (comprising the Pt1 lone pair and Pt1-P bonding pair) to the antibonding Si (Si1).
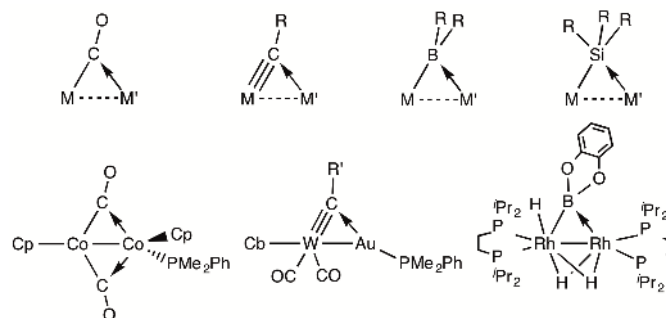
Scheme 4. Ligands with semi-bridging character (Cb = η⁵-C₂B₉H₉Me₂).[17-19]

Simultaneously a strong interaction was, however, observed due to donation from the other Si atom (Si2 lone pair) to the antibonding orbital of the Pt2 centre. This further supports the Si1-Pt1-Pt2-Si2 canonical bonding configuration. For **4** and **5**, the bonding manifolds are essentially similar. The orbital most like a Ni–Ni σ-bond in **5** corresponds to the rather low energy HOMO-12.
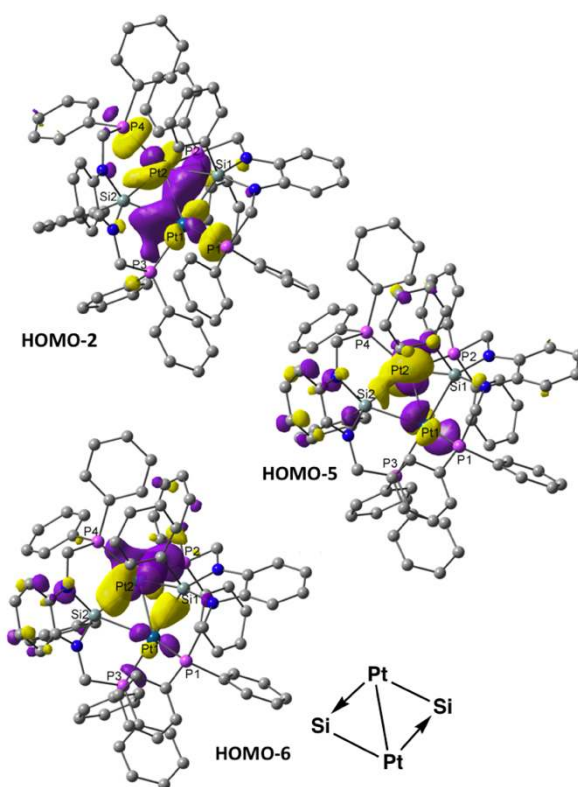

Figure 2. Molecular orbitals of interest relating to the Pt₂Si₂ core of **6.** HOMO-6 corresponds to a Pt→Si dative interaction.

Natural bond orbital (NBO) analysis suggests that the metal-metal bond order increases on going from **5** (0.4) through **4** (0.6) to a maximum with **6** (0.9), the latter two being mirrored in the experimentally determined bond contraction for **6** (2.7200(3) Å) *cf.* **4** (2.788(1) Å). (r_{cov}(Pd) = 1.39, r_{cov}(Pt) 1.36 Å).

In conclusion, both experimental and computational results support the presence of dative M→Si bonding in semi-bridging σ-silyl ligands (devoid of 3c,2e Si–H–M supplementation) and demonstrate that its efficacy endures down a triad.

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