

Covalent palladium–zinc bonds and their reactivity†

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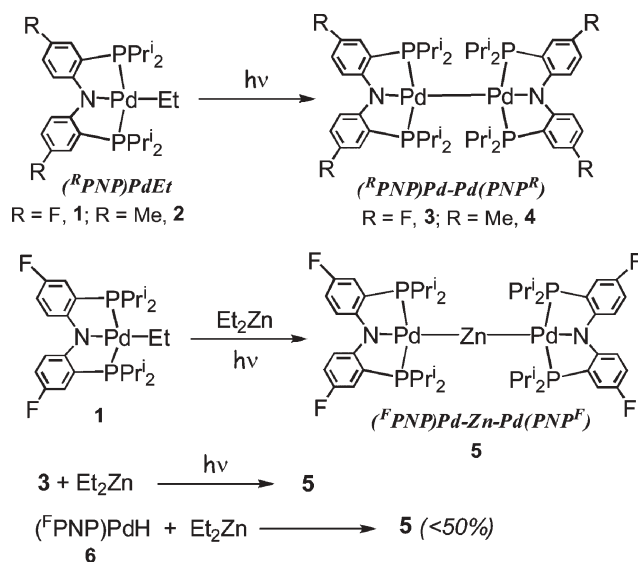
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Photolysis of (^FPNP)Pd–Et in the presence of Et₂Zn leads to the formation of (^FPNP)Pd–Zn–Pd(PNP^F), the first example of a compound with a covalent Pd–Zn bond.

Chemical bonds are the fabric of chemistry. Bonds between many combinations of elements in the periodic table have been described, yet a number of possible element–element bonds still await discovery. Covalent bonds between various transition metals and zinc have been previously reported.^{1–4} Several examples involving bonds between early transition metals (groups 4 and 5) and zinc are known.¹ The majority of the rest contain bonds between Zn and a group 6–9 metal fragments that carry (with some exceptions)⁴ multiple CO ligands,² including Zn[Co(CO)₄]₂,^{2a} the first such reported compound. Compounds with Zn–Zn bonds have also been reported recently.³ A distinctly different group of complexes with M–Zn interactions is comprised of adducts of divalent zinc compounds (ZnX₂) as Lewis acids with transition-metal Lewis bases.⁵ To the best of our knowledge, no example of a Pd–Zn bond has been reported. The lack of prior Pd–Zn examples is particularly interesting given the notoriety of the Negishi coupling of organozinc reagents with aryl halides catalyzed by Pd complexes.⁶ In this Communication we report a well-defined example of compound containing a covalent Pd–Zn bond that was discovered in the course of our studies of the complexes of rigid PNP pincer-type ligands.^{7,8}

We have recently reported that UV irradiation of **1** or **2** leads to the formation of dipalladium dimers **3** and **4** with a single metal–metal bond (Scheme 1).⁹ **3/4** display interesting reactivity, for instance, splitting the NH₃ molecule into a terminal hydride and a terminal amide. Here we report that irradiation of **1** in the presence of Et₂Zn leads instead to a new and unusual compound (**5**) that possesses two covalent Pd–Zn bonds.

Photolysis of **1** in the presence of >1 equiv. Et₂Zn leads to >85% conversion to **5** (NMR evidence). **5** can be isolated in 74% yield (based on Pd). Photolysis of **1** with lower quantities of Et₂Zn leads to a mixture of **3** and **5**. Irradiation ostensibly serves to cleave the Pd–C and the Zn–C bonds in a homolytic fashion. UV homolysis of Zn–C bonds in dialkylzinc compounds has been documented,¹⁰ including in the context of making transition metal–zinc bonds.^{2j} The exact nature of the selectivity leading to the high yield of **5** is not clear. Intermediate formation of **3** is not a problem for the formation of (and perhaps a pathway to) **5** since, in a separate experiment, **5** can be produced (88%, NMR evidence) by photolysis of isolated **3** in the presence of 1 equiv. of Et₂Zn. **5** can also be produced by reacting (PNP)PdH (**6**) with Et₂Zn. In



Scheme 1 Photolysis and other approaches to complex **5**.

this case, **5** is only produced in <50% yield as part of a mixture of several compounds. Notably, **3** does not react with metallic Zn dust, even at 65 °C in THF.

Complex **5** is an orange solid, thermally stable in C₆D₆ solution under argon. Solutions of **5** give rise to NMR spectra with time-averaged D_{2d} symmetry (local C_{2v} symmetry for each PNP fragment) at 22 °C on the NMR timescale, similar to **3**.⁹ A single ³¹P NMR resonance is observed at δ 53.9 ppm and a single ¹⁹F NMR resonance at δ –134.2 ppm, consistent with D_{2d} symmetry.

The solid-state structure of **5** was determined in the course of an X-ray study (Fig. 1).[‡] The Pd–Zn–Pd linkage is linear (as it lies on the two-fold axis). The environment about Pd is approximately square-planar with the Pd atom in plane with the P, N and P atoms of the ^FPNP ligand. The two planes defined by the P, N and P atoms are close to perpendicular (the P1–Pd1–Pd2–P2 dihedral is 86.01(6)°). The structure does not show the distortions of the PNP ligand observed in **4**,⁹ the conformation of the ^FPNP ligand and the environment about Pd in **5** is similar to the sterically unencumbered (^FPNP)PdMe (**7**, Fig. 2).¹¹ Presumably, the separation of the two PNP ligands in **5** is sufficiently large that the steric repulsion between the two PNP ligands is not severe.

From the previously reported structure of (^FPNP)PdMe (**7**)¹¹ and the 0.77 Å covalent radius of CH₃, it is possible to estimate the covalent radius of (^FPNP)Pd at 1.29 Å. Similarly, from the determination of the structure of Me₂Zn,¹² the covalent radius of 1.16 Å for divalent zinc in a linear environment can be extracted. This predicts a covalent Zn–Pd bond length of 2.45 Å. The observed Pd–Zn distances in **5** (2.3793(10) and 2.3723(10) Å) are

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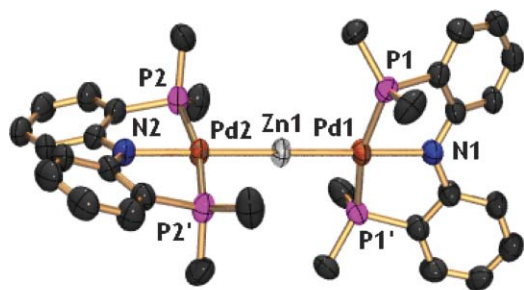


Fig. 1 ORTEP drawings (50% thermal ellipsoids) of **5** with selected atom labeling. H, F atoms as well as Me groups are omitted for clarity. Primed atoms are related to unprimed by a crystallographic C_2 axis passing through atoms N2–Pd2–Zn1–Pd1–N1.

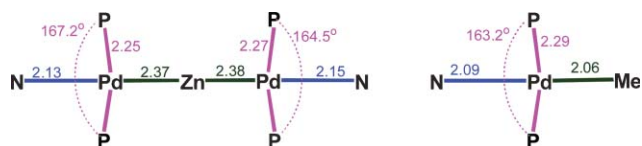
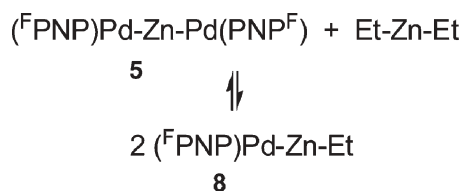


Fig. 2 Metric parameters from the structure of **5** and of $(F)PNP)PdMe$ (**7**). Esds lie in the range of 0.001–0.005 Å and 0.01–0.06°.

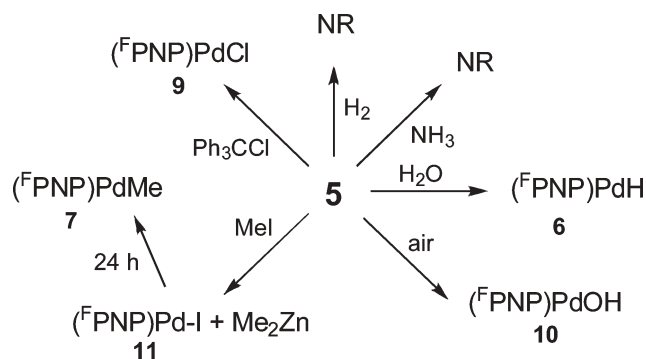
slightly (*ca.* 0.07 Å) shorter than this calculated value, consistent with a covalent single Pd–Zn bond. The Pd–Zn distance in **5** is also considerably shorter than the Pd–Zn distance in the ZnPd alloy (2.65 Å).¹³

In the initial stages of the photolysis of a mixture of **1** and Et_2Zn , we have observed an intermediate (^{19}F NMR (C_6D_6): δ –133.8; $^{31}P\{^1H\}$ NMR (C_6D_6): δ 61.7 ppm) that ostensibly evolves into **5**. We tentatively assign this compound as $(F)PNP)Pd-Zn-Et$ (**8**, Scheme 2). The same compound can be obtained *in situ* upon allowing **5** to react with Et_2Zn . The fraction of **8** increases with the increasing concentration of Et_2Zn , presumably owing to the establishment of the Schlenk-type equilibrium¹⁴ shown in Scheme 2. Removal of volatiles (which includes Et_2Zn) leaves only **5**, thus precluding isolation of **8** in a pure form. A similarly behaving pair of compounds $[CpMo(CO)_3]_2Zn$ and $CpMo(CO)_3-ZnEt$ in equilibrium with Et_2Zn was reported by Thorn in 1991.^{2f}

Since **5** possesses two Pd–Zn bonds, one might formally view this compound as a potential four-electron reductant and expect its reactivity be governed by the drive for the formation of ZnX'_2 and $(PNP)PdX''_2$ products (Scheme 3). Indeed, **5** reacts with >4 equiv. of Ph_3CCl to cleanly produce $(F)PNP)PdCl$ (**9**) (as well as Gomberg's dimer¹⁵ and presumably $ZnCl_2$). Exposure of a C_6D_6 solution of **5** to room air at ambient temperature leads primarily to the formation of $(F)PNP)PdOH$ (**10**) after 24 h. Thermolysis of **5** with 35 equiv. of H_2O in THF (6 h, 95 °C) leads to the clean formation of $(F)PNP)PdH$ (**6**). Unlike **3/4**,⁹ **5** does not react with



Scheme 2 Schlenk-type equilibrium for the Pd–Zn compounds **5** and **8**.



Scheme 3 Reactions of **5**.

NH_3 or H_2 at 95 °C in C_6D_6 . **5** displays rather unexpected reactivity towards MeI. Allowing **5** to react with 2 equiv. of MeI at 22 °C initially leads to *ca.* 90% formation of $(F)PNP)PdI$ (**11**) and Me_2Zn . When this mixture is allowed to stand for 5 d, **11** is slowly methylated to increase the content of $(F)PNP)PdMe$ (**7**) to *ca.* 60%. **11**/ Me_2Zn are thus kinetically preferred products. It is perhaps surprising that the less electronegative carbon partner in Me–I is selectively coupled with the less electronegative partner (Zn) in the Pd–Zn bond in **5**. In contrast, $(CO)_5Mn-Zn-Mn(CO)_5$ was reported to react with MeI to give only Me–Mn(CO)₅.^{2d,e} Addition of MeI across the Pd–Zn bond may be formally regarded as an example of binuclear oxidative addition.¹⁶ On the other hand, the valence¹⁷ of Pd in **5**, **7** or **11** and of Zn in **5**, Me_2Zn or ZnI_2 remains 2 and the reaction can also be formally viewed as a metathesis of single, covalent bonds.

In summary, we report the first example of a compound containing a covalent Pd–Zn bond. Structural studies are consistent with the presence of a single covalent Pd–Zn bond. Reactions of this compound (**5**) generally lead to square planar $(F)PNP)PdX$ complexes.

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Notes and references

‡ Crystal data for **5**,^{18–20} $C_{48}H_{68}F_4N_2P_4Pd_2Zn_1$, $M = 1151.15$, monoclinic, space group: $C2/c$; $a = 22.7195(17)$, $b = 16.3813(9)$, $c = 18.0772(10)$ Å, $\beta = 127.920(6)^\circ$; $U = 5307.4(7)$ Å³; $Z = 4$; $D_c = 1.441$ g cm^{–3}, $T = 294$ K, $\mu(Mo-K\alpha) = 1.286$ mm^{–1}, prismatic habit, orange, $0.14 \times 0.14 \times 0.24$ mm. Data collected on an Enraf-Nonius CAD-4 Turbo diffractometer, $R = 0.0395$; $R_w = 0.0340$ [3161 data, $I > 1.96\sigma(I)$, 278 parameters], $R_w = 0.0666$ (structure factor calculation for all 5385 unique data). CCDC 651085. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b709364k. Selected distances (Å) and angles (°): Pd1–P1 2.2684(13), Pd1–Zn1 2.3793(10), Pd1–N1 2.149(5), Pd2–P2 2.2545(12), Pd2–N2 2.133(5), Pd2–Zn1 2.3723(10); P1–Pd1–P1' 164.48(6), P2–Pd1–P2' 167.19(6).

§ Created using Persistence of Vision Ray Tracer (POV-Ray, <http://www.povray.org/>) and Ortep-3 for Windows.²¹

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