

The chelate-to-bridging shift of phosphane dipalladacycles: Convenient synthesis of double A-frame tetranuclear complexes.

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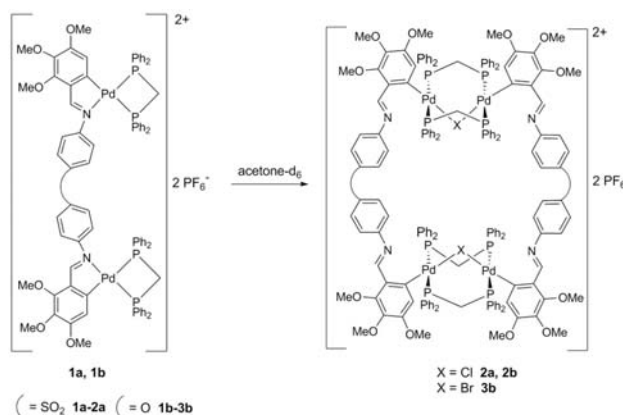
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Palladacycles of the type [Pd₂(Ph₂PCH₂PPh₂-P,P)₂(C,N:C,N)] (C,N:C,N = bis(*N*-2,3,4-trimethoxybenzylidene)-4,4'-sulfonyldianiline or -4,4'-oxydianiline) can undergo a spontaneous slow chelate-to-bridging diposphane coordination shift in solution. Following this strategy a tailor-made synthetic procedure was devised that culminates in isolation of double A-frame tetranuclear palladium complexes.

The chemistry of cyclometallated compounds¹ has attracted much research interest in past years. They are known for their ample applications in numerous fields: organic synthesis,² photochemistry,³ catalysis,⁴ and as potential biologically active materials.⁵ We now report a chelate-to-bridging shift which occurs spontaneously in solution even at low temperature in palladacycles bearing Ph₂PCH₂PPh₂-P,P, (dppm), with formation of double A-frame complexes; systems that are related to the field of supramolecular coordination complexes (SCCs).⁶ For the complexes reported herein the choice of tetranuclear species as opposed to the isomeric 1D-polymeric forms results from the experimental data. In the absence of adequate mass spectra, where crystal structure determination was possible the SCC metallacycle structure arised.⁷ We have previously described formation of an A-frame complex stemming from a chelated dppm palladacycle.⁸ We reasoned that there could be a conversion between both species with the latter being the kinetically stable isomer. This strategy should open up a convenient access to supramolecular palladacycles *via* attachment of more than one A-frame arrangement in the multinuclear complex. In an initial attempt at this task the dinuclear palladacycles with phenylenediimine-

C,N:C,N failed to undergo this conversion,⁸ most probably due to the restricted flexibility of the ligand imposed by the rigidity of the central phenylene ring itself, hindering opening of the metallacycle ring needed to provide the extra vacant coordination site on the metal for the second incoming phosphane ligand. We then hypothesized that in order to fix the A-frame disposition a more favorable environment was needed. In this regard we envisioned more flexible bidentate nitrogen-donor ligands able to supply the needed coordination adaptability of the metal centers and sufficient room to accommodate the phosphane donors, for which purpose bis(*N*-2,3,4-trimethoxybenzylidene)-4,4'-sulfonyldianiline, **a**, or -4,4'-oxydianiline, **b**, were chosen. Accordingly, what follows is our synthetic strategy for making double A-frame tetranuclear palladium structures based on non-rigid bidentate imines appropriate for dimetallation bearing -SO₂- and -O- spacers (Scheme 1).



Scheme 1. Reaction sequence leading to the synthesis of the double A-frame complexes. The chlorido and bromido ligands come from **Ila**, **Iib** (Cl) and **IIb** (Br) (see ESI).

During the NMR determination of **1a** in CDCl₃ we observed that signals other than those expected seemed to slowly dawn in the ¹H NMR spectrum of **1a** ca. 4.0 ppm suggesting a new species was developing. Then, the CDCl₃ NMR tube solution of **1a** was left to stand, whereupon single-crystals appeared; an

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X-ray crystallographic analysis showed them to be compound **2a**: a novel tetranuclear palladium(II) double A-frame framework bearing two palladium pairs, each bridged by a $\{(\mu\text{-PCP})_2/\mu\text{-Cl}\}$ group, in support of our hypothesis that a less rigid imine architecture should allow spanning of the diphosphanes across the metal centers.

As for the choice of **2a** versus **1a** it should be noted that two opposing factors concur. On the one hand, favoring **1a** is the thermodynamic stability associated with two chelate rings at palladium: the five- and four-membered metallacycle and phosphane rings, respectively, whilst none in **2a**; on the other one, the strain imposed by the four-membered chelate ring should favor ring opening, enabling intermediates with uncoordinated phosphorus donors, which coupling together should yield the bridging system. Also, the presence of the stronger Pd–P as compared to the Pd–N bond in terms of Pearson's concept,⁹ supports **2a**.

In view of these results and to further clarify this situation we proceeded to approach an analogous study and the related ligand **b** was considered. Our ensuing hypothesis was that the resulting solution of **1b** should give rise to **2b** over time, provided that some Cl[−] ion from the precursor remains in solution. Notwithstanding, **1b** was kept at very low temperature, *c.a.* −40 °C, to avoid the **1b**→**2b** shift when running the first ¹H and ³¹P NMR. On approaching *r.t.*, *c.a.* −10 °C, conversion already begins, **1b** slowly transforming into **2b** with time at room temperature. Figure 1 depicts changes over a five day period; inspection of the HC=N and MeO resonances puts forward the steady evolution. Left to stand compound **2b** precipitates as neat single crystals, thus completing the transformation. Attempts to prepare **2a** or **2b** directly from the parent halide-bridged complexes (see ESI) with dpdm was not possible; the reaction always proceeds through the chelated species, which then undergoes conversion to **2a** or **2b**.

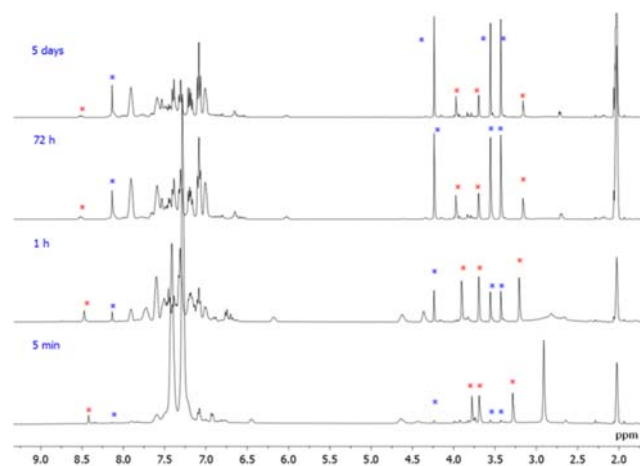


Figure 1. Time-dependent ¹H NMR plot for the **1b**→**2b** shift at *r.t.* Compound **1b**,*. Compound **2b**,*.

Then, the synthesis of **2a** was carried out in acetone-*d*₆ in a similar fashion to **2b** in order to elucidate whether or not a chlorinated solvent provides the chlorido ligands. The result was that once again **1a** furnishes **2a** and a similar time-

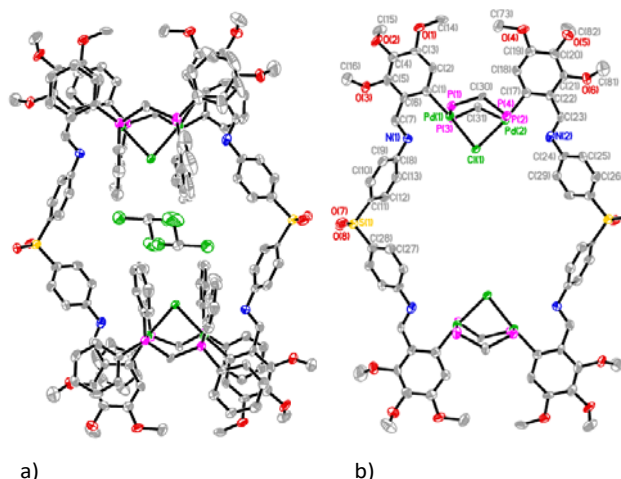


Figure 2. a) Thermal ellipsoid plot of the cation for **2a** shown at 30% probability level, inclusive of CDCl₃ solvent molecules. b) Labelling scheme for the asymmetric unit. Hydrogen atoms and phosphane phenyls (in b) have been omitted for clarity. Selected bond distances (Å) and angles (deg) for **2a**: Pd(1)–C(1) 1.996(9), Pd(1)–Cl(1) 2.452(2), Pd(1)–P(1) 2.334(3), Pd(1)–P(3) 2.342(3), Pd(2)–C(1) 2.416(2), Pd(2)–C(17) 2.002(10), Pd(2)–P(2) 2.299(3), Pd(2)–P(4) 2.326(3), C(1)–Pd(1)–P(1) 88.9(3), C(1)–Pd(1)–P(3) 87.8(3), P(1)–Pd(1)–Cl(1) 92.6(1), P(3)–Pd(1)–Cl(1) 91.54(1).

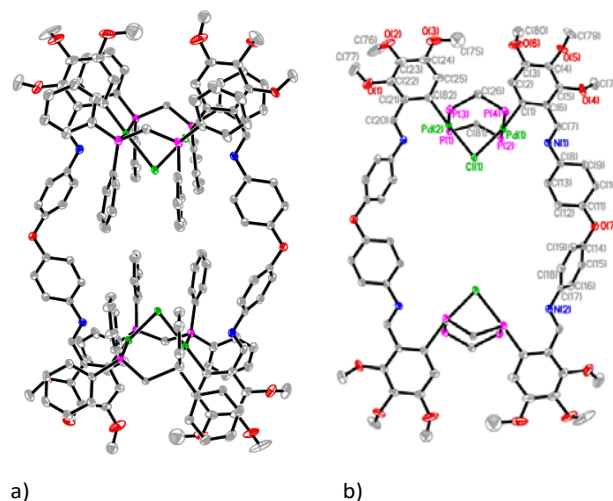


Figure 3. a) Thermal ellipsoid plot of the cation for **2b** shown at 30% probability level. Solvent molecules removed for clarity. b) Labelling scheme for the asymmetric unit. Hydrogen atoms and phosphane phenyls (in b) have been omitted for clarity. Selected bond distances (Å) and angles (deg) for **2b**: Pd1–C1 1.997(4), Pd1–P2 2.3228(8), Pd1–P4 2.3331(9), Pd1–Cl1 2.4328(8), Pd2–C82 1.994(4), Pd2–P1 2.3569(9), Pd2–P3 2.3168(9), Pd2–Cl1 2.4607(9), C(1)–Pd(1)–P(2) 84.98(10), C(1)–Pd(1)–P(4) 85.96(10), P(2)–Pd(1)–Cl(1) 93.40(3), P(4)–Pd(1)–Cl(1) 94.58(3).

dependent ^1H NMR plot as depicted in Figure 1 was obtained for the $1\text{a} \rightarrow 2\text{a}$ shift (Figure 1ESI). Although at this point it then seemed clear that the chlorido ligand stemmed from the parent halide-bridged compounds and not from the solvent, we sought to prepare the analogous A-frame bromido complex to ascertain this, as well as to show that the shift may be extended to other bridging halides. Thus, in a similar experiment 3b was obtained (ESI), as a tetranuclear compound with two $\{\text{Pd}\mu\text{-Br}(\mu\text{-PPh}_2\text{CH}_2\text{PPh}_2)_2\text{Pd}\}$ groups. Figure 4 shows the ORTEP view for the molecule of 3b .

The crystal structures of complexes 2a , 2b and 3b provide unequivocal evidence of the $1\text{a} \rightarrow 2\text{a}$, $1\text{b}(\text{IIb}) \rightarrow 2\text{b}$ and $1\text{b}(\text{IIIb}) \rightarrow 3\text{b}$ conversion processes, and the reproducibility of the preparation routine, of which to the best of our knowledge there are no reported examples. Figures 2, 3 and 4 show the ORTEP view of the molecules of 2a , 2b and 3b , respectively (see ESI). Each asymmetric unit (half-cation of the complex) may be described as formed by two approximately square-planar palladium centers bonded through two dpmp and one chlorido or bromido bridging ligands. The organic ligands are then linked by four Pd–C bonds to the two $\{\text{Pd}\mu\text{-X}(\mu\text{-PPh}_2\text{CH}_2\text{PPh}_2)_2\text{Pd}\}$ ($\text{X} = \text{Cl}, \text{Br}$) frameworks to envisage a cavity which, where appropriate, hosts the disordered chloroform-d1 (2a) and acetone-d6 (2b) molecules.

The bond distances are within the expected values with allowance for lengthening of the Pd–Cl and Pd–Br bonds due to the high *trans* influence of the metallated phenyl carbon atom.

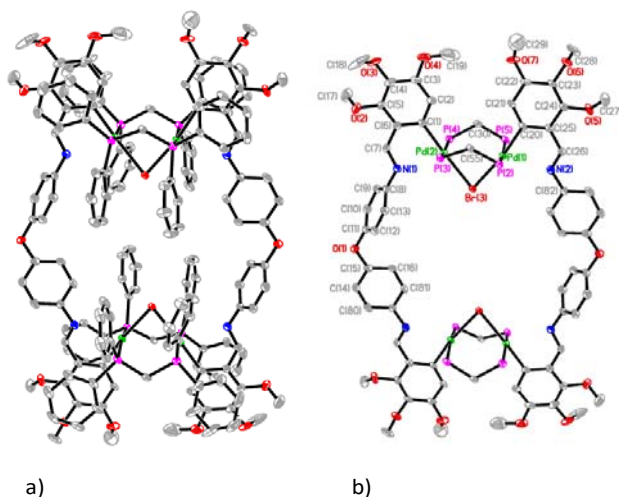


Figure 4. a) Thermal ellipsoid plot of the cation for 3b shown at 30% probability level. Solvent molecules removed for clarity. b) Labelling scheme for the asymmetric unit. Hydrogen atoms and phosphane phenyls (in b) have been omitted for clarity. Selected bond distances (Å) and angles (deg) for 3b : Pd1–C20 2.006(4), Pd1–P2 2.3237(10), Pd1–P5 2.3338(11), Pd1–Br3 2.5459(5), Pd2–Br3 2.5722(6), C(20)–Pd(1)–P(2) 85.06(11), C(20)–Pd(1)–P(5) 85.55(11), P(2)–Pd(1)–Br(3) 93.90(3), P(5)–Pd(1)–Br(3) 94.24(3).

The Pd–N distances *ca.* 2.79(1) Å (2a), 2.74 Å (2b) and 2.72 Å (3b) suggest weak Pd \cdots N interactions as previously observed in the range 2.576(4)–2.805(5) Å¹⁰ pointing towards a

pseudo-penta-coordination at palladium. The eight-membered $\text{Pd}(\mu\text{-PCH}_2\text{P})_2\text{Pd}$ rings adopt a *pseudo*-boat conformation, with the two methylene groups and the bridging chlorido (2a , 2b) or bromido (3b) lying on opposite faces of the Pd_2P_4 plane. The nearly co-planar metallated phenyl rings are essentially perpendicular to the Pd_2P_4 plane, presumably in order to minimize repulsions with the dpmp phenyl rings; π - π stacking interactions between the phosphane phenyl rings cooperate to stabilize the structure. Analogous interactions between dpmp and the aromatic rings of the ditopic linkers are not likely, due lack of parallelism between the phenyl rings and to the distances between centroids (ESI). The P–C–P angles *ca.* 116.6° (2a), 115–117° (2b) and (3b) 116–118° are larger than the value of 106.4° reported for the uncoordinated dpmp ligand,¹¹ probably due to steric requirements to form the main core of the A-frame structure. The Pd–Pd distances of 3.254 Å (2a), 3.173 Å (2b) and 3.222 Å (3b) preclude any metal–metal interactions.

A DFT analysis was performed for the compounds 1b and 2b using the package of programs g09.¹² In order to compare the relative stability between the chelate (1b , which present two conformers) and the A-frame (2b) forms described here, some distances and angles are also compared to explain the difference in energy (see ESI). The reported geometry and frequency calculations were carried out at the B3LYP/LANL2DZ-ECP¹³/6-31g(d) level of theory and no imaginary frequencies were found, confirming the stationary points.

The results indicate that the equilibrium between the two forms is displaced towards ($\Delta G = -171$ Kcal/mol) the A-frame conformation that is in agreement with the crystal structure obtained and the NMR studies performed on the reaction solution. The A-frame compound is more stable because the palladium environment is less constrained due to opening of the C–C=N and P–C–P angles, (Δ *ca.* 4° and 16°, respectively). Moreover, the chelate effect is neutralized by the formation of a supramolecular cage that is more stable from an entropic point of view. Figure 5 depicts a graphical representation of the relative energies of the compounds under study.

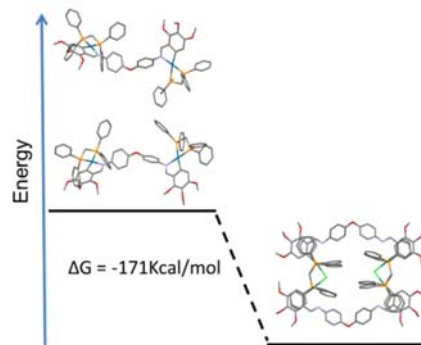


Figure 5. Representation of the differing energies for the chelated and the A-frame compounds.

In summary, we have designed a unique synthetic route for achieving double A-frame assemblies from multinuclear

halide-bridged palladacycles *via* dinuclear chelated phosphane intermediates. This result represents a further enrichment in the chemistry of palladacycles SCCs as well as in the coordination chemistry of dpmm; the crystal structures representing unambiguous evidence of the chelating to bridging dpmm shift. Although our examples have thus far been with dpmm it seems likely that other systems will show the phenomenon and that care should be taken in the choice of palladacycle and phosphane. For instance, preliminary tests show that PPh₂PN(Me)PPh₂ strongly favors chelation in terms of the *gem*-dimethyl effect,¹⁴ stabilizing the di-chelated compound, thus stopping the shift.

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Conflicts of interest

There are no conflicts to declare.

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