

## Electronic Supplementary Information

### Unusual reactivity of a sterically hindered diphosphazane ligand, EtN{P(OR)<sub>2</sub>}<sub>2</sub>, (R = C<sub>6</sub>H<sub>3</sub>(Pr<sup>i</sup>)<sub>2-2,6</sub>) towards (η<sup>3</sup>-allyl)palladium precursors

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#### 1. Comments on the reactivity of L towards [(1,3-R,R'-η<sup>3</sup>-C<sub>3</sub>H<sub>3</sub>)Pd(μ-Cl)]<sub>2</sub> R = H, R' = Me; R = H, R' = Ph; R = R' = Me; R = R' = Ph;

The reaction of [Pd(1-Me-η<sup>3</sup>-C<sub>3</sub>H<sub>4</sub>)(μ-Cl)]<sub>2</sub> with (L) in the presence of NH<sub>4</sub>PF<sub>6</sub> gives the cationic complex [(1-Me-η<sup>3</sup>-C<sub>3</sub>H<sub>4</sub>)Pd(L)](PF<sub>6</sub>) (**5**) which exists as two isomers as shown by its <sup>31</sup>P {<sup>1</sup>H}NMR spectrum. The spectrum showed three broad resonances at δ<sub>p</sub> 113.0, 110.7 and 109.3 ppm at 293 K. At 183 K, these were partially resolved into two sets of resonances which could be assigned to *syn*- and *anti*- isomers of the cationic complex (**5**). The relative abundance of the *anti*- isomer (~ 40 %) is higher than that observed for the related palladium allyl complex of [(1-Me-η<sup>3</sup>-C<sub>3</sub>H<sub>4</sub>)Pd(P-P)]PF<sub>6</sub>, (P-P) = [MeN{P(OR)<sub>2</sub>}<sub>2</sub>], (R = C<sub>6</sub>H<sub>3</sub>Me<sub>2-2,6</sub>) reported recently.<sup>[1]</sup> However, catalytic studies could not be carried out using the cationic complex (**5**) owing to its instability.

The diphosphazane ligand (L) did not react with di-μ-chloro-bis(1,3-dimethyl-η<sup>3</sup>-allyl)dipalladium [Pd(1,3-Me-η<sup>3</sup>-C<sub>3</sub>H<sub>4</sub>)(μ-Cl)]<sub>2</sub>, di-μ-chloro-bis(1-phenyl-η<sup>3</sup>-allyl)dipalladium [Pd(1-Ph-η<sup>3</sup>-C<sub>3</sub>H<sub>4</sub>)(μ-Cl)]<sub>2</sub> and di-μ-chloro-bis(1,3-diphenyl-η<sup>3</sup>-allyl)dipalladium [Pd(1,3-Ph-η<sup>3</sup>-C<sub>3</sub>H<sub>4</sub>)(μ-Cl)]<sub>2</sub> under analogous reaction conditions. The free ligand resonance (δ<sub>p</sub>: 151.0 ppm, s) was intact even after stirring the reaction mixture for 24 h in acetone at 298 K. On the other hand, heating the reaction mixture

under reflux produced considerable amount of ligand monoxide ( $\delta_P$ : 144.0 d,  $-1.7$  d,  $^2J_{PP} = 49$  Hz).

## 2. A discussion on the torsion angles observed in dinuclear Pd(I) complexes of diphosphazanes

Besenyi *et. al.* have noted that the metal–metal bond lengths in dipalladium complexes bearing bridging diphosphines decrease with an increase in the dihedral angle between the two metal coordination planes.<sup>[2]</sup> Selected structural data for complexes (2), (6) and other dinuclear Pd(I) complexes containing bridging diphosphazane ligands are given in Table S1. With the lone exception of  $\text{Pd}_2\text{Cl}_2\{\text{P}(\text{OCH}_2\text{CF}_3)_2\text{NMe}\}_2$  ( $\phi = 2.8^\circ$ ), the dihedral angle between the two coordination planes around the palladium atoms approaches the ideal value of  $45^\circ$ , which minimizes repulsive interaction of the out-of-plane metal  $d\pi$  orbitals on adjacent metal centers. Although rotation around the metal–metal bond is restricted by the bridging nature of the 'P-N-P' ligand, the steric repulsions of ligands *cis* to the M–M bond is presumably less in the case of diphosphonite ligands owing to oxygen spacers which link the phenyl rings to the 'P-N-P' skeleton. Complexes (2) and (6) cannot be compared with the other complexes listed in Table S1 because they contain only one 'P-N-P' ligand bridging the two metal centers. The large steric bulk of the ligand L precludes the formation of a complex containing two bridging diphosphazane ligands. The available data on 'P-N-P' based systems is insufficient to derive any relationship between  $\phi$  and the metal-metal bond length.

**Table S1** Selected bond lengths and torsion angles in Pd complexes containing a bridging diphosphazane ligand

Entry	Compound	Pd–Pd	Pd–P <sup>b</sup>	Pd–Cl	( $\phi$ ) <sup>c</sup>
1	Complex <b>2</b>	2.531(1)	2.164[2]	–	46.3
2	Complex <b>6</b>	2.576(1)	2.198[1]	2.316(1)	40.6
3	Pd <sub>2</sub> Cl <sub>2</sub> (dppa) <sub>2</sub> .CH <sub>3</sub> CN <sup>a</sup>	2.635(1)	2.287[2]	2.398[2] <sup>b</sup>	42.6
4	Pd <sub>2</sub> Cl <sub>2</sub> (dppa) <sub>2</sub> .CH <sub>3</sub> COCH <sub>3</sub> <sup>a</sup>	2.638(1)	2.279[1]	2.407 [1] <sup>b</sup>	36.8
5	Pd <sub>2</sub> Cl <sub>2</sub> {(P(OPh) <sub>2</sub> ) <sub>2</sub> NPh} <sub>2</sub> <sup>a</sup>	2.620(1)	2.260[2]	2.374[2] <sup>b</sup>	37.0
6	PdCl <sub>2</sub> {(P(OCH <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub> ) <sub>2</sub> NMe} <sub>2</sub> <sup>a</sup>	2.629(1)	2.259[2]	2.395[2] <sup>b</sup>	2.8

<sup>a</sup>For details see ref [3, 4]; dppa = HN(PPh<sub>2</sub>)<sub>2</sub>. <sup>b</sup>Average distance of all Pd–P/ Pd–Cl bonds;  
<sup>c</sup>Dihedral angle between the two metal coordination planes.

### 3. The crystal structure analysis of [Pd( $\mu$ -Cl){P(O)(OR)<sub>2</sub>}{P(OR)<sub>2</sub>(NH*Et*)}]<sub>2</sub>, (**4**)

The molecular structure of complex (**4**) is shown in Figure S1. Selected bond distances and bond angles are listed in Table S2. Complex (**4**) is a neutral, chloride bridged dinuclear Pd(II) species, formed by the loss of both the allyl fragments of the precursor complex [Pd( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)( $\mu$ -Cl)]<sub>2</sub>. Two molecules of the ligand [EtN{P(OC<sub>6</sub>H<sub>3</sub>(Pr<sup>i</sup>)<sub>2</sub>-2,6)<sub>2</sub>}<sub>2</sub>] (**L**) have undergone hydrolytic cleavage of the P–N bond to give P(O)((OC<sub>6</sub>H<sub>3</sub>(Pr<sup>i</sup>)<sub>2</sub>-2,6))<sub>2</sub> and P(NH*Et*)(OC<sub>6</sub>H<sub>3</sub>(Pr<sup>i</sup>)<sub>2</sub>-2,6)<sub>2</sub> moieties which are bonded to the two Pd centers in such a way that they are oriented trans to each other across the Pd<sub>2</sub>( $\mu$ -Cl)<sub>2</sub> unit. The Pd–Cl bond lengths (2.394(3)–2.445(3) Å) fall within the range of values observed for similar complexes with a Pd<sub>2</sub>( $\mu$ -Cl)<sub>2</sub> core.<sup>[5]</sup> The average P–O aryl bond distance (1.604(8) Å) is slightly shorter than that (1.650(5) Å) observed for the free ligand **L**. The P(4)–O(10) (1.482(8) Å) and the P(2)–O(5) (1.477(8) Å) bond distances are considerably shorter as would be expected for a P=O bond and are close to that observed for P=O bond (1.458 (2) Å) in the ligand monoxide (**L'**). The short N(1)...O(5) and N(2)...O(10) separations (2.684 Å, 2.673 Å) suggest the presence of an

intramolecular N–H...O hydrogen bond ( $\angle\text{N}(1)\text{--H}(1)\dots\text{O}(5) = 128.0^\circ$ ;  $\angle\text{N}(2)\text{--H}(2)\dots\text{O}(10) = 135.1^\circ$ ).

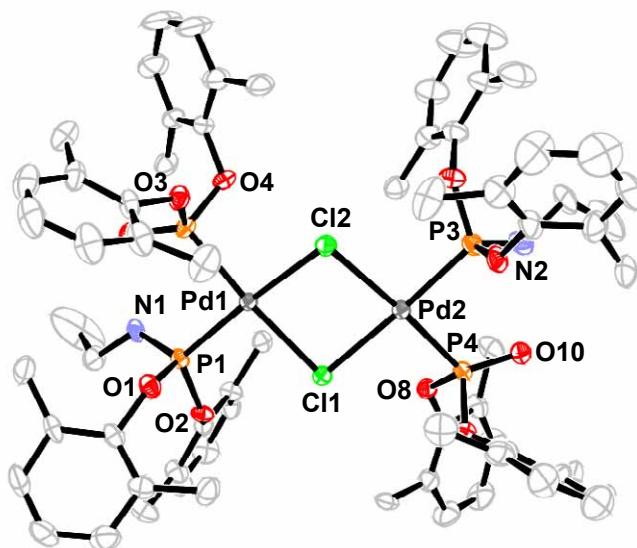


Figure S1. The ORTEP plot of complex (4); the atoms are represented by their vibrational ellipsoids of 30% probability.

## 2. The crystal structure analysis of ligand monoxide [EtN{P<sup>III</sup>(OC<sub>6</sub>H<sub>3</sub>(Pr<sup>i</sup>)<sub>2-2,6</sub>)<sub>2</sub>}{P<sup>V</sup>(O)(OC<sub>6</sub>H<sub>3</sub>(Pr<sup>i</sup>)<sub>2-2,6</sub>)<sub>2</sub>}] (L')

The solid-state structure of ligand (L') is shown in Figure S2. Selected bond distances and angles are listed in Table S2. The geometry around the nitrogen atom is trigonal planar with a P–N–P angle of 120.81(9)° which is much larger than that (109.5(5)°) observed for the free ligand L.<sup>[6]</sup> The P–N and P–O bond distances are consistent with the literature reports.<sup>[1, 3, 6]</sup> The ligand adopts a conformation in which the lone pair on the P<sup>III</sup>(OR)<sub>2</sub> phosphorus is oriented *trans* to the ethyl group on the nitrogen atom whereas the P=O oxygen of the P<sup>V</sup>(O)(OR)<sub>2</sub> fragment is *cis* to it. The P<sup>III</sup>–N and P<sup>V</sup>–N distance bond distances are 1.706(2) Å and 1.661(2) Å respectively in (L'), whereas the P–N bond distance in the unoxidized ligand (L) is 1.674(5) Å. This difference in P–N bond lengths in (L') can be explained on the basis of the “negative hyperconjugation” model.<sup>[7]</sup> The

two phenyl rings on each phosphorus atom are almost orthogonal ( $\sim 85^\circ$ ) to each other owing to the steric bulk of the isopropyl substituents at the ortho positions.

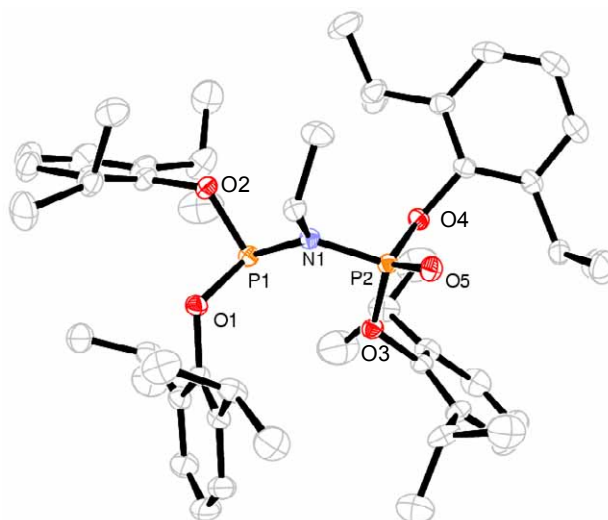


Figure S2. The ORTEP plot of ligand monoxide (L'); the atoms are represented by their vibrational ellipsoids of 30% probability.

Table S2. Selected bond distances (Å) and angles (°) for (4) and (L')

<b>[Pd(<math>\mu</math>-Cl){P(O)(OR)<sub>2</sub>}{P(OR)<sub>2</sub>(NHEt)}]<sub>2</sub>, (4)</b>			
Bond Lengths (Å)			
Pd(1)...Pd(2)	3.551	P(2)–O(4)	1.610(8)
Pd–Cl $\langle \rangle$	2.419[3]	P(2)–O(5)	1.477(8)
Pd–P $\langle \rangle$	2.253[3]	P(3)–O(6)	1.610(8)
P(1)–N(1)	1.611(9)	P(3)–O(7)	1.601(8)
P(3)–N(2)	1.602(10)	P(4)–O(8)	1.605(8)
P(1)–O(1)	1.597(7)	P(4)–O(9)	1.606(8)
P(1)–O(2)	1.599(8)	P(4)–O(10)	1.482(8)
P(2)–O(3)	1.603(8)	N(1)...O(5)	2.678
		N(2)...O(10)	2.685
Bond Angles (°)			
N(2)–H(2)...O(10)	135.1	P(1)–Pd(1)–P(2)	90.78(11)
N(1)–H(1)...O(5)	128.0	P(4)–Pd(2)–P(3)	91.32(11)
<b>[EtN{P<sup>III</sup>(OC<sub>6</sub>H<sub>3</sub>(Pr<sup>i</sup>)<sub>2</sub>,6)<sub>2</sub>}{P<sup>V</sup>(O)(OC<sub>6</sub>H<sub>3</sub>(Pr<sup>i</sup>)<sub>2</sub>,6)<sub>2</sub>}] (L')</b>			
Bond Lengths (Å)			
P(1)–O(1)	1.6534(15)	C(25)–N(1)	1.510(2)
P(1)–O(2)	1.6415(16)	P(2)–O(3)	1.5891(15)
P(1)–N(1)	1.7062(18)	P(2)–O(4)	1.5979(15)
P(2)–N(1)	1.6614(17)	P(2)–O(5)	1.4577(15)
Bond Angles (°)			
O(1)–P(1)–O(2)	96.20(8)	O(5)–P(2)–O(3)	118.48(8)
O(3)–P(2)–O(4)	100.43(8)	O(5)–P(2)–O(4)	113.54(9)
		P(1)–N(1)–P(2)	120.81(9)

## References

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