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Unusual reactivity of a sterically hindered diphosphazane ligand, $EtN\{P(OR)_2\}_2$, (R = $C_6H_3(Pr^i)_2$-2,6) towards (η^3-allyl)palladium precursors†‡

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The reactivity of (η^3-allyl)palladium chloro dimers $[(1\text{-R-}\eta^3\text{-}C_3H_4)PdCl]_2$ (R = H or Me) towards a sterically hindered diphosphazane ligand $[EtN\{P(OR)_2\}_2]$ (R = $C_6H_3(Pr^i)_2$-2,6), has been investigated under different reaction conditions. When the reaction is carried out using NH_4PF_6 as the halide scavenger, the cationic complex $[(1\text{-R-}\eta^3\text{-}C_3H_4)Pd\{EtN(P(OR)_2)_2\}]PF_6$ (R = H or Me) is formed as the sole product. In the absence of NH_4PF_6, the initially formed cationic complex, $[(\eta^3\text{-}C_3H_5)Pd\{EtN(P(OR)_2)_2\}]Cl$, is transformed into a mixture of chloro bridged complexes over a period of 4 days. The dinuclear complexes, $[(\eta^3\text{-}C_3H_5)Pd_2(\mu\text{-}Cl)_2\{P(O)(OR)_2\}\{P(OR)_2(NHEt)\}]$ and $[Pd(\mu\text{-}Cl)\{P(O)(OR)_2\}\{P(OR)_2(NHEt)\}]_2$ are formed by P–N bond hydrolysis, whereas the octa-palladium complex $[(\eta^3\text{-}C_3H_5)(2\text{-Cl-}\eta^3\text{-}C_3H_4)Pd_4(\mu\text{-}Cl)_4(\mu\text{-}EtN\{P(OR)_2\}_2)]_2$, is formed as a result of nucleophilic substitution by a chloride ligand at the central carbon of an allyl fragment. The reaction of $[EtN\{P(OR)_2\}_2]$ with $[(\eta^3\text{-}C_3H_5)PdCl]_2$ in the presence of K_2CO_3 yields a stable dinuclear (η^3-allyl)palladium(I) diphosphazane complex, $[(\eta^3\text{-}C_3H_5)[\mu\text{-}EtN\{P(OR)_2\}_2Pd_2Cl]$ which contains a coordinatively unsaturated T-shaped palladium center. This complex exhibits high catalytic activity and high TON's in the catalytic hydrophenylation of norbornene.

Introduction

The reaction of (η^3-ally1)palladium complexes with nucleophiles to afford allylic alkylation products is of wide ranging synthetic utility.[1] One of the most significant aspects of this chemistry is the prospect of controlling the chemo-, regio-, stereo- and enantioselectivity of the nucleophilic attack on the allyl moiety through appropriate choice of the reaction conditions and the ancillary ligands attached to palladium.[2] As a result, there is considerable current interest in investigating the electronic and steric interactions that govern the selectivity in catalytic transformations proceeding through (η^3-allyl)palladium intermediates.

A recent report by Mandal *et al.* has shown that the reaction of a sterically bulky diphosphazane ligand $[MeN\{P(OR)_2\}_2]$ (R = $C_6H_3Me_2$-2,6), with $[(1,3\text{-}Me_2\text{-}\eta^3\text{-}C_3H_3)Pd(\mu\text{-}Cl)]_2$ and $[(1\text{-Me-}\eta^3\text{-}C_3H_4)Pd(\mu\text{-}Cl)]_2$, resulted in a mixture of isomers, of which the normally less favored *syn*/*anti* isomer (in the former case) and the *anti*-isomer (in the latter case) were present to a greater extent than that observed for other diphosphazane ligands. This result has been attributed to the steric interactions between the allyl moiety and the diphosphazane ligand which partly destabilizes the *syn*-isomer.[3] If the relative proportion of the *anti*-isomer is increased, the reaction with nucleophiles might result in an increased amount of *Z*-substitution products in allylic alkylation reactions.[4] Hence, we reasoned that introducing more bulky substituents in the auxiliary diphosphazane ligand might further enhance the relative proportion of the *anti*-isomer. As an initial step towards this goal, we set out to explore the reactivity of (η^3-allyl)palladium chloro dimers towards the sterically encumbered diphosphazane ligand $[EtN\{P(OR)_2\}_2]$, (R = $C_6H_3(Pr^i)_2$-2,6) *viz.*, (**L**) under various experimental conditions. In addition to the expected cationic allyl palladium complexes, several unusual products have been isolated and their structures established by single crystal X-ray diffraction studies.

Results and discussion

The reaction of $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ with (**L**) in the presence of NH_4PF_6 as the chloride scavenger gives the cationic complex $[(\eta^3\text{-}C_3H_5)Pd(\mathbf{L})](PF_6)$ (**1a**) as the sole product. This complex could be isolated in a pure form and characterized by C, H, N elemental analysis and NMR spectroscopic data. The same reaction in the absence of NH_4PF_6 initially gives the cationic complex $[(\eta^3\text{-}C_3H_5)Pd(\kappa^2\text{-}\mathbf{L})]Cl$ (**1b**) analogous to complex (**1a**) as shown by the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture. The spectrum shows a single resonance at δ_P 111.0 ppm; this chemical shift is close to that observed for complex (**1a**). Efforts to isolate this complex were unsuccessful. It was found to be highly sensitive to air and moisture, and over a period of 96 h was slowly transformed

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† The HTML version of this article has been enhanced with colour images.

‡ Electronic supplementary information (ESI) available: Reactivity of (**L**) towards substituted (η^3-allyl) palladium chloro dimers, a comparison of bondlengths and torsion angles in diphosphazane bridged palladium complexes, structural details of complex (**4**) and ligand monoxide (**L′**). See DOI: 10.1039/b703308g

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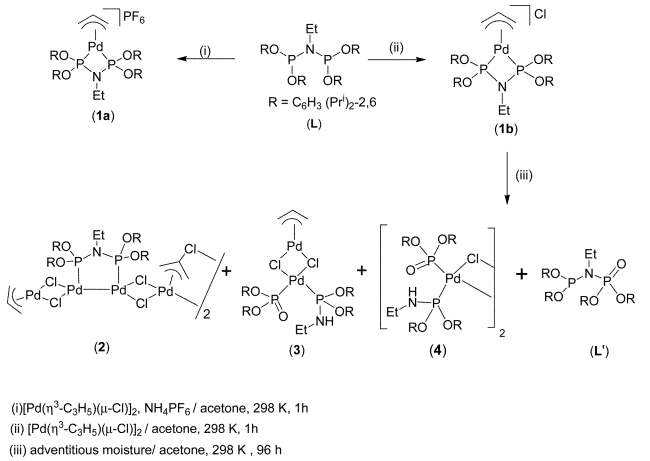
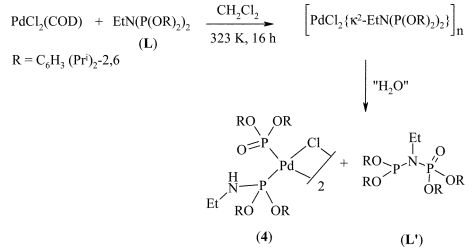
into a mixture of complexes (**2**), (**3**), (**4**) and the ligand monoxide (**L′**) (Scheme 1). In addition, two unidentified products with resonances at δ_P 65.0 and 130.3 ppm were found in the reaction mixture. The structures of complexes (**2**), (**3**) and (**4**) have been established by single crystal X-ray diffraction studies. These products are formed apparently by hydrolysis, reduction or oxidation. Even though the reaction was carried out under an atmosphere of dry nitrogen, traces of moisture present in the glass surface or ingress of moisture during crystallization led to the formation of these products. The synthetic procedures were optimized to obtain complexes (**2**), (**3**) and (**4**) (See Experimental section).



Scheme 1 Reaction of $[EtN\{P(OR)_2\}_2]$, (R = C_6H_3 $(Pr^i)_2$-2,6) (**L**) with $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)]_2$.

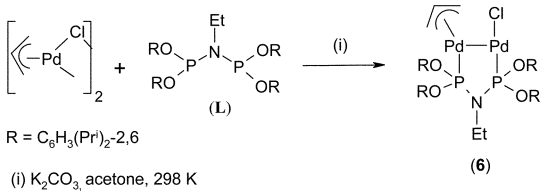
The most remarkable product obtained in the reaction of $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ and ligand (**L**) is the octa-palladium complex, $[(\eta^3\text{-}C_3H_5)(2\text{-}Cl\text{-}\eta^3\text{-}C_3H_4)Pd_4(\mu\text{-}Cl)_4(\mu\text{-}EtN\{P(OR)_2\}_2)]_2$, (**2**) formed as a result of nucleophilic substitution at the central allyl carbon of one of the allyl fragments. The $^{31}P\{^1H\}$ NMR spectrum of (**2**) displays a sharp singlet at δ_P 98.0 ppm. The first report on nucleophilic attack at the central allyl carbon of a transition metal (η^3-allyl) complex was by Green and coworkers in 1976.[5] Since then, there are several reports of similar reactivity in transition metal (π-allyl) complexes of Mo, W, Pt, Pd, Mn, Zr, Ti, Ir and Rh.[6] The anions that act as nucleophiles in these reactions include malonate and enolate-type anions, simple alkyl (*e.g.*, RLi, RMgX) or hydride reagents (*e.g.*, $NaBH_4$).[7] Despite the fact that Cl^- is one of the simplest available species for nucleophilic attack in synthetically useful palladium catalysed transformations, examples of chloride migration in (η^3-allyl)palladium complexes are rare. Szabo has reported the first theoretical study complemented by experimental verification on ligand assisted chloride migration in (η^3-allyl) palladium complexes.[8] There is only one other example in the literature of chloride migration from a palladium center to the allylic carbon terminus.[9] To our knowledge, complex (**2**) represents the first example of nucleophilic attack by a chloride ligand at the central carbon atom of a (η^3-allyl) palladium complex. A clear understanding of the regiochemistry of nucleophilic attack at the central allyl carbon observed in complex (**2**) calls for detailed theoretical investigations.[6,10]

The chloro bridged dinuclear Pd(II) diphosphazane complexes $[(\eta^3\text{-}C_3H_5)Pd_2(\mu\text{-}Cl)_2\{P(O)(OR)_2\}\{P(OR)_2(NHEt)\}]$, (**3**) and $[Pd(\mu\text{-}Cl)\{P(O)(OR)_2\}\{P(OR)_2(NHEt)\}]_2$, (**4**) are formed as a result of hydrolytic cleavage of the P–N bond of the diphosphazane ligand and loss of one or more allyl fragments. The $^{31}P\{^1H\}$ NMR spectra of complexes (**3**) and (**4**) are of the AX type; the chemical shift of $\{P(OR)_2(NHEt)\}$ (86.4 or 78.8 ppm) lies downfield from that of $\{P(O)(OR)_2\}$ (32.1 or 29.1 ppm). An alternate route to complex (**4**) involves the reaction of $[PdCl_2(COD)]$ and $[EtN\{P(OR)_2\}_2]$ (**L**) in dichloromethane at 323 K for 16 h (Scheme 2). The initial product gives rise to a sharp singlet at δ_P 65.0 ppm, which has been tentatively assigned to the complex $[PdCl_2(\kappa^2\text{-}\mathbf{L})]_n$, since the δ_P value lies in the range normally observed for a chelating diphosphazane ligand.[11] Allyl complexes of phosphoramidites such as complexes (**1**) and (**3**) are rare in the literature. Recently, Pregosin *et al.* have reported the structures and solution dynamics of several mono-phosphoramidite and bis-phosphoramidite 2-methallyl and 1,3-diphenylallyl complexes of palladium.[12]



Scheme 2 An alternate synthetic procedure for complex (**4**).

The unique reactivity of the ligand (**L**) prompted us to investigate the base-induced reduction of $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ precursor in the presence of (**L**). Base-induced reduction of Pd(II) complexes to give Pd(0) species in the presence of phosphine ligands is well documented in the literature.[13] The significance of such reactions lies in the involvement of Pd(0) species in various catalytic transformations. A palladium(0) species is implicated in numerous catalytic reactions, including carbon–carbon and carbon–heteroatom cross-coupling and carbonylation reactions.[14] When the reaction between $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ and (**L**) was carried out in the presence of K_2CO_3 in acetone at 298 K in open atmosphere, the coordinatively unsaturated palladium(I) complex $[(\eta^3\text{-}C_3H_5)[\mu\text{-}(EtN\{P(OR)_2\}_2)Pd_2Cl]$ (**6**) was obtained in 70% yield (Scheme 3). The orange–red crystalline compound was found to be remarkably stable over a period of 12 months when stored in a closed vial. The reaction of diphosphazane ligands $[MeN\{P(OR)_2\}_2]$ (R = C_6H_5 or $C_6H_3Me_2$-2,6) with (η^3-allyl)palladium chloride dimers are known to form ligand-bridged dinuclear Pd(I) complexes by the reduction of Pd(II) to Pd(I) and the loss of the allyl fragment.[3,15]



Scheme 3 Synthesis of the dinuclear three-coordinated Pd(I) complex (**6**).

Allyl palladium complexes of diphosphazane ligands bearing phenoxy substituents are relatively rare in the literature because

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of their high π-acidity owing to the presence of two electronegative oxygen atoms attached to each phosphorus center.[3] The high π-acceptor nature of (**L**) combined with its large steric bulk destabilizes the cationic complex $[(\eta^3\text{-}C_3H_5)Pd(\kappa^2\text{-}\mathbf{L})]Cl$ (**1b**), making it susceptible for the loss of the (η^3-allyl) fragment which triggers the subsequent reactions. Apparently, the chloride ion released during the initial bridge-splitting reactions to form the cationic complex (**1b**) acts as the chloride source for nucleophilic substitution to yield complex (**2**). The steric strain imposed by the bulky diphosphazane ligand **L** in complex (**1b**) is released during P–N bond rupture, and this acts as the driving force for the formation of complexes (**3**) and (**4**). Similar solvolytic cleavage of diphosphazane ligands bound to transition metals by water or protic solvents has been reported.[16,17]

Single crystal X-ray diffraction studies

The solid-state structures of $[(\eta^3\text{-}C_3H_5)(2\text{-}Cl\text{-}\eta^3\text{-}C_3H_4)Pd_4(\mu\text{-}Cl)_4(\mu\text{-}EtN\{P(OR)_2\}_2)]_2$ (**2**), $[(\eta^3\text{-}C_3H_5)Pd_2(\mu\text{-}Cl)_2\{P(O)(OR)_2\}\{P(OR)_2(NHEt)\}]$ (**3**), $[Pd(\mu\text{-}Cl)\{P(O)(OR)_2\}\{P(OR)_2(NHEt)\}]_2$ (**4**), $[(\eta^3\text{-}C_3H_5)[\mu\text{-}(EtN\{P(OR)_2\}_2)Pd_2Cl]$ (**6**) and the ligand monoxide (**L′**) have been determined by X-ray crystallography. The salient structural features of complexes (**2**), (**3**) and (**6**) only are discussed below. The crystal and molecular structures of complex (**4**) and the diphosphazane ligand monoxide (**L′**) are discussed in the ESI.‡

Crystal and molecular structure of $[(\eta^3\text{-}C_3H_5)(2\text{-}Cl\text{-}\eta^3\text{-}C_3H_4)Pd_4(\mu\text{-}Cl)_4(\mu\text{-}EtN\{P(OR)_2\}_2)]_2$ (2). The ORTEP plot of complex (**2**) is shown in Fig. 1. Selected bond distances and angles are listed in Table 1. The molecular framework consists of two tetra-palladium units with an inversion center at the midpoint of a six-membered ring, *viz.*, Pd(1)–C(52)–Cl(1)–Pd(1′)–C(52′)–Cl(1′). The asymmetric unit consists of a tetra-palladium chain in which the adjacent metal centers are bridged by either two chloride ligands or the bidentate diphosphazane ligand in an alternating fashion. The terminal metal atoms of the asymmetric unit (Pd1 and Pd4) are capped by two allyl fragments bound in an η^3-mode. The dihedral angle between the square plane containing the allyl carbon atoms, and the plane containing the 'Pd(μ-Cl)$_2$' unit bound to it, is ~120°.

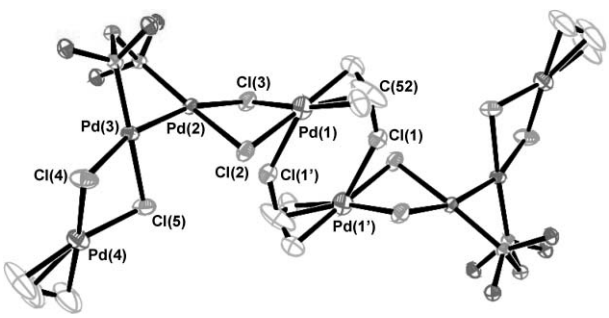

Fig. 1 The ORTEP view of the basic framework in complex (**2**). The atoms are represented by their vibrational ellipsoids of 30% probability. All carbon atoms except those of the allyl fragment, all hydrogen atoms, the water molecule and acetone present in the lattice have been omitted for clarity. The prime in Pd(1′) indicates that this atom is at (1 − *x*, 1 − *y*, −*z*).

Table 1 Selected bond distances and angles for complex (**2**)

$[(\eta^3\text{-}C_3H_5)(2\text{-}Cl\text{-}\eta^3\text{-}C_3H_4)Pd_4(\mu\text{-}Cl)_4(\mu\text{-}EtN\{P(OR)_2\}_2)]_2$, (**2**)

Bond lengths/Å			
Pd(1) ··· Pd(2)	3.356	Pd(2)–Cl(3)	2.4270(19)
Pd(2)–Pd(3)	2.5309(9)	Pd(3)–Cl(4)	2.420(2)
Pd(3) ··· Pd(4)	3.413	Pd(3)–Cl(5)	2.443(2)
Pd(1) ··· Pd(1′)[a]	3.554	Pd(4)–Cl(5)	2.376(2)
Pd(1)–Cl(1′)	2.476(2)	Pd–P<>	2.1644[17]
Pd(1)–Cl(2)	2.410(2)	C(52)–Cl(1)	1.53(2)
Pd(1)–Cl(3)	2.425(2)	$(C\text{–}C)_{allyl}$ <>	1.35[3]
Pd(2)–Cl(2)	2.442(2)	$Pd\text{–}C_{allyl}$ <>	2.13[12]

Bond angles/Torsion angles/°	
P(1)–N(1)–P(2)	111.9(3)
Cl(3)–Pd(2)–Pd(3)–Cl(4)	67.11(8)
P(1)–Pd(2)–Pd(3)–P(2)	46.26(6)

[a] Pd(1′) indicates that this atom is at (1 − *x*, 1 − *y*, −*z*).

A remarkable feature of the molecule is that the two tetra-palladium units are bridged by two chloro allyl moieties. Nucleophilic substitution occurs at C(52) of one allyl fragment (Fig. 1), and this chloride coordinates to an adjacent palladium center giving rise to a six-membered ring structure; the Pd(1) ··· Pd(1)′ separation is 3.554 Å. The two 'Pd(μ-Cl)$_2$Pd' mean planes flanking the 'Pd(μ-**L**)Pd' unit are nearly orthogonal (dihedral angle: 87°) as a result of the huge steric bulk of the diphosphazane ligand (**L**). Consequently, the terminal $(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)_2$ mean plane subtends an angle of 63° with the $(2\text{-}Cl\text{-}\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)_2$ mean plane of the same asymmetric unit. This steric factor is also reflected in the P(1)–Pd(2)–Pd(3)–P(2) torsion angle of 46.26(6)° spanned by (**L**) across the Pd(2)–Pd(3) bond. The bridging 'P–N–P' ligand holds the two metal centers together with a short M–M bond distance of 2.5309(9) Å. This distance is shorter than the M–M bond distances observed for dimeric Pd(I) complexes containing bridging diphosphazanes.[11,18,19] The twist along the Pd–Pd axis is attributed to the anti-bonding interactions of filled metal d-orbitals that are minimized when the torsion angle equals 45°.[20] The five-coordinate palladium adopts a distorted square pyramidal geometry with a chloride ligand occupying the axial coordination site. The crystal lattice also contains one molecule of water and one molecule of acetone. The water oxygen atom O(6) shows a weak interaction with the Pd(4) atom (Pd(4)–O(6) distance 2.51(3) Å).

Crystal and molecular structure of $[(\eta^3\text{-}C_3H_5)Pd_2(\mu\text{-}Cl)_2\{P(O)(OR)_2\}\{P(OR)_2(NHEt)\}]$ (3). The molecular structure of complex (**3**) is shown in Fig. 2. It consists of a neutral, chloro bridged dinuclear species capped by an η^3-allyl fragment at one terminus (Fig. 2). The ligand $[EtN\{P(OR)_2\}_2]$, (R = $C_6H_3(Pr^i)_2$-2,6), (**L**) has apparently undergone P–N bond rupture followed by hydrolysis to form $P(O)(OR)_2$ and $P(NHEt)(OR)_2$ moieties which are bound to palladium. Selected bond distances and angles are listed in Table 2. The P(1)–N(1) bond distance (1.615(3) Å) is less than that (1.674(5) Å) observed for the ligand (**L**).[21] The geometry around the metal centers is essentially planar. The dihedral angle between the square plane containing the allyl carbon atoms, and

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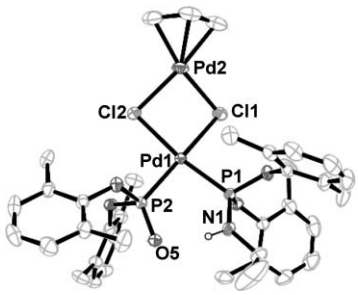

Fig. 2 The ORTEP plot of complex (**3**). The atoms are represented by their vibrational ellipsoids of 30% probability. The CH_3 carbon atoms of the isopropyl groups and all hydrogen atoms (except the NH proton) have been omitted for clarity.

Table 2 Selected bond distances and angles for complex (**3**)

$[(\eta^3\text{-}C_3H_5)Pd_2(\mu\text{-}Cl)_2\{P(O)(OR)_2\}\{P(OR)_2(NHEt)\}]$, (**3**)			
Bond lengths/Å			
Pd(1)···Pd(2)	3.358	N(1)–P(1)	1.615(3)
Pd–Cl <>	2.4003[11]	P(1)–O(1)	1.601(3)
Pd–C_{allyl} <>	2.107[5]	P(1)–O(2)	1.611(3)
Pd(1)–P(1)	2.2385(10)	P(2)–O(3)	1.609(3)
Pd(1)–P(2)	2.2516(10)	P(2)–O(4)	1.610(3)
N(1)···O(5)	2.708	P(2)–O(5)	1.482(3)
Bond angles/°			
N(1)–H(1)···O(5)	158	Cl(1)–Pd(2)–Cl(2)	87.17(4)
P(1)–Pd(1)–P(2)	93.77(4)	Cl(2)–Pd(1)–P(2)	93.55(4)
P(1)–Pd(1)–Cl(1)	87.59(4)	Cl(1)–Pd(1)–Cl(2)	85.75(4)

the plane containing the 'Pd(μ-$Cl)_2$' unit bound to it, is ~102°. The N–H proton is hydrogen bonded to O(5), the O(5)···N(1) distance being 2.708 Å (∠O(5)–H(1)–N(1) = 158°). The average P–O (aryl) single bond distance (1.608(1) Å) is slightly reduced when compared to that (1.650(5) Å) in the free ligand (**L**). The P(2)–O(5) bond distance is 1.482(3) Å as would be expected for a P=O bond.

Crystal and molecular structure of [(η^3-C_3H_5)]μ-(EtN{P-($OR)_2$}$_2$)Pd_2Cl] (6). The molecular structure of complex (**6**) (shown in Fig. 3) consists of a bimetallic Pd(I) unit bridged by the diphosphazane ligand, (**L**). The allyl fragment is bonded to one palladium center in an η^3-fashion thereby coordinatively saturating it, whereas the other tri-coordinate Pd(I) center is bonded to a chloride. The dihedral angle between the plane containing the allyl carbon atoms and the plane containing the 'Pd–P–N–P' unit bound to it, is ~167°. The geometry around the low-coordinate palladium is essentially T-shaped with a P(1)–Pd(1)–Cl(1) angle measuring 174.71(4)° which is more linear compared to the P(1)–Pd–N angle in the 14e T-shaped Pd(II) complexes of the type [(4-MeO–C_6H_4)Pd(PBu^t_2R)(N((3,5-$CF_3)_2C_6H_3)_2$)] (R = Bu^t, ferrocenyl, or 1′,2′,3′,4′,5′-pentaphenyl-1-ferrocenyl), reported by Yamashita and Hartwig.[22] There are no agostic interactions; the hydrogen atom H(7) (attached to C(7)), which is nearest to Pd(1), is at a distance of 2.932 Å from the metal center. The average P–N bond distance (1.691(8) Å) is slightly longer than that (1.674(5) Å) observed in the free ligand (**L**). The Pd(1)–P(1) bond is shorter than the Pd(2)–P(2) bond (see Table 3). The five-membered

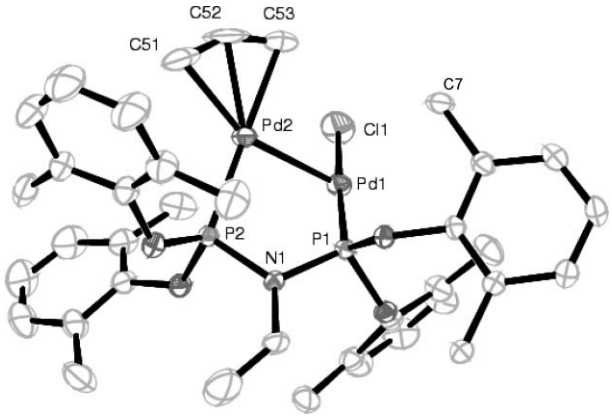

Fig. 3 The ORTEP plot of complex (**6**). The atoms are represented by their vibrational ellipsoids of 30% probability. The hydrogen atoms, CH_3 carbon atoms of isopropyl groups and acetone present in the lattice have been omitted for clarity.

Table 3 Selected bond distances and angles for complex (**6**)

(η^3-C_3H_5)Pd_2Cl(μ-EtN{$P(OR)_2$}$_2$), (**6**)			
Bond lengths/Å			
Pd(1)–Cl(1)	2.3158(13)	P(2)–O(4)	1.615(3)
Pd(1)–Pd(2)	2.5755(7)	P(1)–N(1)	1.698(3)
P(1)–Pd(1)	2.1376(10)	P(2)–N(1)	1.685(3)
P(2)–Pd(2)	2.2588(11)	N(1)–C(25)	1.485(5)
P(1)–O(1)	1.625(2)	C(51)–Pd(2)	2.180(6)
P(1)–O(2)	1.635(3)	C(52)–Pd(2)	2.112(6)
P(2)–O(3)	1.620(3)	C(53)–Pd(2)	2.169(5)
Bond angles/Torsion angles/°			
P(1)–N(1)–P(2)	112.89(17)		
O(1)–P(1)–O(2)	98.41(13)		
O(3)–P(2)–O(4)	100.66(15)		
P(1)–Pd(1)–Pd(2)–P(2)	40.63(4)		

ring comprising the two palladium atoms and the PNP skeleton adopts a 'half-chair' conformation with one of the palladium atoms slightly projecting out of the mean plane. The coordination geometry around each metal is approximately planar, but the two metal coordination planes are twisted so that the P(1)–Pd(1)–Pd(2)–P(2) torsion angle is 40.63(4)°, thereby minimizing the anti-bonding interactions of filled metal d-orbitals.[20,23] The twisted conformation also allows the ligands to span a shorter metal–metal bond. The remarkable stability of the three-coordinate complex can be attributed to the steric crowding imposed by the bulky ligand **L** at the unsaturated palladium center. A discussion of Pd–Pd bond distances and torsion angles observed in complexes (**2**), (**6**) and other dinuclear Pd(I) complexes of diphosphazanes is given in the ESI.‡

Catalytic studies using the coordinatively unsaturated complex (6). Coordinatively unsaturated organopalladium(II) complexes are often proposed as intermediates in metal-mediated organic transformations such as C–C bond forming reactions,[24] hydroamination,[25] etherification,[26] and Stille coupling reactions,[27] and hence have attracted considerable scientific interest. Sterically encumbered phosphine ligands that can facilitate the formation of

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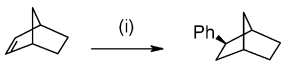
catalytically active low coordinate species are well known in the literature.[28] To the best of our knowledge, there are no studies so far using T-shaped complexes as catalysts in homogenous hydrophenylation reactions. Complex (**6**) exhibits extremely high turnover numbers (TON's) in catalytic homogeneous hydroarylation reaction (hydrophenylation of norbornene with iodobenzene)[29] even when aerobic conditions are employed. Carbon–carbon coupling in the presence of NEt_3/formic acid as hydride source and catalytic amounts of (**6**) gives *exo*-phenylnorbornane in quantitative yield (isolable yield: 98%) (Scheme 4). TON's of 2.07×10^6 are obtained even when the catalyst loading is as low as 4.8×10^{-5} mol%. Catalytic hydrophenylation could not be achieved using a 1 : 1 molar ratio of $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)]_2$ and the ligand $[EtN\{P(OR)_2\}_2]$ (**L**) as catalyst instead of complex (**6**).



(i) PhI, Et_3N, HCO_2H, cat.**6**,
12 h, DMSO, 393 K

Scheme 4 Hydrophenylation of norbornene catalyzed by complex (**6**).

Conclusions

In conclusion, we have shown for the first time that nucleophilic attack by a chloride ligand can take place at the central carbon atom of a (π-allyl)palladium complex. We also present here the first example of a dinuclear Pd(I) complex containing a sterically encumbered diphosphazane, which displays a true three-coordinate T-shaped geometry at one Pd center, and demonstrates its potential as an efficient hydroarylation catalyst under aerobic conditions. Because of its high stability and ready accessibility, the T-shaped complex offers a wide scope for studying small molecule insertion reactions across the Pd(I)–Pd(I) bond.[30] The reactivity of (η^3-allyl)palladium precursors with other "P–N–P" type ligands under various reaction conditions warrants further study.

Experimental

General details

The NMR spectra were recorded in $CDCl_3$ using a Bruker Avance-400 spectrometer with Me_4Si as an internal standard for ^1H and ^{13}C NMR measurements and 85% H_3PO_4 as an external standard for ^{31}P NMR measurements. Chemical shifts downfield from the standard were assigned positive values. Infrared spectra were recorded using a Perkin-Elmer Model 457 spectrometer. Elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyzer. Triethylamine and petrol (bp 60–80 °C) were purified by conventional procedures and freshly distilled prior to use. DMSO was distilled over CaH_2, and stored over molecular sieves. Unless noted otherwise, acetone was distilled over $KMnO_4$ and used without further drying. The precursor complexes $[Pd(1\text{-}Me\text{-}\eta^3\text{-}C_3H_4)(\mu\text{-}Cl)]_2$ and $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$,[31] and the ligand (**L**), $[EtN\{P(OR)_2\}_2]$[21] were prepared according to published procedures.

Preparation of $[(\eta^3\text{-}C_3H_5)Pd\{EtN(P(OC_6H_3(Pr^i)_2\text{-}2,6)_2)_2\}]PF_6$ (1a). The ligand $[EtN\{P(OR)_2\}_2]$ (**L**) (0.223 g, 2.74×10^{-4} mol) was added to a solution of $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)]_2$ (0.050 g, 1.37×10^{-4} mol) and NH_4PF_6 (0.045 g, 2.74×10^{-4} mol) in dry acetone (20 mL, distilled twice from K_2CO_3) at 25 °C. The reaction mixture was stirred at room temperature for 2 h and was filtered to remove the precipitated ammonium chloride. Solvent was evaporated from the reaction mixture and acetone (5 mL) added. The solution was layered with petrol. Colorless micro-crystals of **1a** were formed over a period of 24 h. Yield: 0.120 g, 79% Anal. Calcd. for $Pd_1F_6P_3O_4\ N_1C_{53}H_{78}$: C, 57.6; H, 7.1; N, 1.3. Found: C, 57.5; H, 7.2; N, 1.2. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.0–1.33 (m, 48H, CH_3 of 2,6-Pr^i), 1.87 (t, 3H, CH_2CH_3, $^3J_{HH} = 7$ Hz), 2.59 (br, 2H, H_a of allyl), 2.9 (br, 2H, H_s of allyl), 3.10–3.17 (m, 8H, C*H* of 2,6-Pr^i), 4.14–4.3 (m, 2H, CH_2CH_3), 5.31 (m, 1H, H_c of allyl), 6.85–7.28(m, 12H, aryl protons). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.9 MHz): δ 111.0, (s). ^{13}C NMR (allyl carbons,* $CDCl_3$, 293 K): 73.9 (dd, {12.5, $^2J(P,C)_{cis}$, 54.1, $^2J(P,C)_{trans}$,} C_t), 124.2 (t, C_c). IR (Nujol, cm^{-1}): 3131(s), 2968 (w), 2873(s), 1587(s), 1464(w), 1437(m), 1255(s), 1100(w), 931, 889, 863, 769, 667, 558, 476. *(C_t: terminal allyl carbon atoms; C_c: central allyl carbon).

Preparation of $[(\eta^3\text{-}C_3H_5)(2\text{-}Cl\text{-}\eta^3\text{-}C_3H_4)Pd_4(\mu\text{-}Cl)_4(\mu\text{-}EtN\{P(OR)_2\}_2)]_2$, (2). The ligand **L** (0.059 g, 0.73×10^{-4} mol) and $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ (0.038 g, 1.04×10^{-4} mol) were introduced into a 100 mL round bottomed flask equipped with a magnetic stirring bar and an inlet for nitrogen. Acetone (20 mL) was added and the reaction mixture was stirred for 96 h. The resultant red–orange solution was filtered in an open atmosphere using a Whatman No. 42 filter paper and the filtrate was evaporated to dryness. The residue was redissolved in a minimum amount of acetone and the solution left aside. Deep red rhombus-shaped crystals of (**2**) were formed over a period of 24 h along with colorless crystals of complexes (**3**), (**4**) and the ligand monoxide (**L′**). The crystals of complex (**2**) were separated by handpicking them from the mother liquor, washed with cold acetone and air-dried. Complex (**2**) was found to be air-stable for a period of 5–6 weeks. Yield: (0.060 g), 20%. Anal. Calcd. for $C_{112}H_{164}N_2O_8P_4Pd_8Cl_{10}.CH_3COCH_3{\cdot}H_2O$ (found): C, 45.2 (45.7); H, 5.6 (5.2); N, 0.9 (1.2). IR (Nujol, cm^{-1}): 3049, 2964, 2870, 1583, 1565, 1456, 1439, 1383, 1327, 1256, 1157, 1092, 913, 874, 762, 734, 662, 438, 405, 368, 305. $^{31}P\{^1H\}$ NMR: δ 98.0, (s). ^{13}C (allyl carbons): 52.5 (s, C_t), 62.2 (s, $C_{t'}$), 110.4 (s, C_c), 206 (s, $C_{c'}$).

Preparation of $[(\eta^3\text{-}C_3H_5)Pd_2(\mu\text{-}Cl)_2\{P(O)(OR)_2\}\{P(OR)_2\text{-}(NHEt)\}]$ (3). The ligand (**L**) (0.111 g, 1.37×10^{-4} mol) was added to a solution of $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)]_2$ (0.050 g, 1.37×10^{-4} mol) in acetone (20 mL) at 25 °C and the reaction mixture stirred for 12 h. Solvent was evaporated to give a foamy yellow solid. Acetone (5 mL) was added and the solution "layered" with petroleum ether. Colorless crystals of **3** were formed over a period of 24 h. Yield: 0.053 g, 40% Anal. Calcd for $Pd_2Cl_2P_2O_5\ N_1C_{53}H_{79}$: C, 55.1; H, 6.9; N, 1.2. Found: C, 55.0; H, 7.1; N, 1.3. ^1H NMR ($CDCl_3$, 400 MHz): δ 0.48 (t, 3H, CH_2CH_3, $^3J_{HH} =$ 7 Hz), 0.99–1.28 (m, 48H, CH_3 of 2,6-Pr^i), 2.59 (m, 2H, H_a of allyl), 2.9 (br, 2H, H_s of allyl), 3.66–3.82 (m, 8H, C*H* of 2,6-Pr^i), 3.9–4.16 (m, 2H, CH_2CH_3), 5.4 (m, 1H, H_c of allyl), 6.95–7.10 (m, 12H, aryl protons), 8.05(br, N*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.9 MHz): δ 86.4 d, (δP_A), 32.1 d, (δP_X), ($^2J_{P\text{-}P} = 99$ Hz). ^{13}C NMR (allyl carbons, $CDCl_3$, 293 K): 69.8 (br, C_t), 116.2 (br, C_c). IR (Nujol, cm^{-1}): 3417(m), 3057(s), 2959(w), 2866(s),

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1922(m), 1713(s), 1586(s), 1463(w), 1154(w), 1091(w), 759(s), 654(w), 578(m), 514(s), 480(w), 451(s).

Preparation of [Pd(μ-Cl){P(O)(OR)$_2$}{P(OR)$_2$(NHEt)}]$_2$ (4). The ligand (**L**) (0.223 g, 2.74 × 10^{-4} mol) was added to a solution of [(η^3-C_3H_5)Pd(μ-Cl)]$_2$ (0.050 g, 1.37 × 10^{-4} mol) in acetone (20 mL) at 25 °C and the reaction mixture stirred for 24 h. The solution was concentrated to ~5 mL and layered with petrol. Colorless crystals of **4** were formed over a period of 24 h. Yield: 0.130 g, 49% Anal. Calcd for $Pd_2Cl_2P_4O_{10}N_2C_{100}H_{148}\cdot 2CH_3COCH_3$: C, 62.8; H, 8.0; N, 1.4. Found: C, 62.6; H, 8.1; N, 1.2. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.32–0.6 (br, 2 × 3H, CH_2CH_3), 0.99–2.07 (m, 2 × 48H, CH_3 of 2,6-Pr^i), 3.02–3.96 (m, 2 × 8H, C*H* of 2,6-Pr^i), 4.96 (m, 2 × 2H, CH_2CH_3), 6.39–7.37 (m, 2 × 12H, aryl protons), 8.33(br, 2 × 1H N*H*). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.9 MHz): δ 78.8 d, (δP_A), 29.1 d, (δP_X), ($^2J_{P\text{-}P}$ = 94 Hz). IR (Nujol, cm^{-1}): 3419(w), 2964(br), 1713(m), 1443(m), 1368(m), 1253(s), 1155(m), 1092(br), 905(br), 758(s), 656(br), 577(m), 514(s), 477(br).

Preparation of [(η^3-C_3H_5)]μ-(EtN{P(OR)$_2$}$_2$Pd$_2$Cl] (6). The ligand (**L**) (0.111 g, 1.37 × 10^{-4} mol) was added to a suspension of [(η^3-C_3H_5)Pd(μ-Cl)]$_2$ (0.050 g, 1.37 × 10^{-4} mol) and K_2CO_3 (0.009 g, 6.85 × 10^{-5} mol) in acetone (20 mL) at 25 °C and the reaction mixture stirred for 6 h during which time the solution turned deep yellow. Solvent was evaporated from the reaction mixture and freshly distilled acetone (10 mL) was added. The solution was passed through a short plug of Celite (7 cm × 2 cm) and concentrated to ~5 mL. Orange crystals of **6** were formed over a period of 24 h. Yield: 0.110 g, 69%. Anal. Calcd for $Pd_2Cl_1P_2O_4N_1C_{53}H_{78}\cdot CH_3COCH_3$: C, 57.9; H, 7.3; N, 1.2. Found: C, 58.0; H, 7.1; N, 1.3. ^{1}H NMR ($CDCl_3$, 293 K): δ 0.92–1.3 (m, 48H, CH_3 of 2,6-Pr^i), 1.85 (t, 3H, CH_2CH_3, $^3J_{HH}$ = 7 Hz), 2.18 (br, 1H, CH_2 of allyl), 3.0 (br, 1H, CH_2 of allyl) 3.25–3.75 (m, 8H, CH of 2,6-Pr^i, 1H, CH_2 of allyl), 4.42 (m, 2H, CH_2CH_3), 4.6 (m, 1H, CH_2 of allyl), 5.2 (m, 1H, CH of allyl), 7.09–7.19 (m, 12H, aryl protons). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): δ 147.6 d, (δP_A), 125.8 d, (δP_B), ($^2J_{P\text{-}P}$ = 188 Hz). ^{13}C NMR (allyl carbons, $CDCl_3$, 293 K): 71.6 (d, *C_t, ^2J(P,C) *trans* = 38 Hz), 117.1 (br, s *$C_{t'}$), 124.2 (br, *C_c). IR (KBr, cm^{-1}): 2962(s), 2868(s), 1713(s), 1460(m), 1324(m), 1253(s), 1153(m), 1088(w), 865(w), 762(s), 671(w). IR (Nujol, cm^{-1}): 588, 515, 406, 387, 297, 209. *(C_t: allyl carbon *trans* to Pd–P bond; $C_{t'}$: allyl carbon *trans* to Pd–Pd bond; C_c: central allyl carbon).

Procedure for the catalytic hydrophenylation of norbornene using iodobenzene

To 5 mL of dry DMSO were added iodobenzene (1 mmol), norbornene (3 mmol), Et_3N (4 mmol), and formic acid (3 mmol). An appropriate amount of catalyst (**6**·CH_3COCH_3), dissolved in 0.5 mL acetone was introduced into the stirred solution. The reaction mixture was maintained at 120 °C for 12 h and allowed to attain room temperature. Water (5 mL) was added and the reaction mixture was extracted with EtOAc (10 mL × 3). The combined organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The product was purified by column chromatography using benzene–petrol (1 : 4 v/v) as the eluant. Phenylnorbornane: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.74–1.27 (m, 8H, CH and CH_2), 2.36 (s, 2H, CH_2), 2.74 (m, 1H, CH), 7.26–7.15 (m, 5H, Ar).

X-Ray crystallography

Crystal data for all the complexes were collected on a BRUKER SMART APEX CCD diffractometer (graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å) using SMART software.[32] The data was integrated with SAINT[33] and an empirical absorption correction was applied using SADABS.[34] The structures were solved by the Patterson method using SHELXS-97 and refined by full-matrix least squares methods against F^2 (SHELXL-97).[35] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms except the NH proton of complex (**3**) were placed in their calculated positions; the NH proton of

Table 4 Summary of X-ray diffraction data for the ligand monoxide (**L′**) and complexes (**2**), (**3**), (**4**) and (**6**)

Compound	Ligand monoxide (**L′**)	Complex (**2**)	Complex (**3**)	Complex (**4**)	Complex (**6**)
Formula	$C_{50}H_{73}N_1O_5P_2$	$C_{115}H_{172}Cl_{10}N_2O_{10}P_4Pd_8$	$C_{53}H_{79}Cl_2N_1O_5P_2Pd_2$	$C_{106}H_{158}Cl_2N_2O_{12}P_4Pd_2$	$C_{56}H_{84}Cl_1N_1O_5P_2Pd_2$
M	830.03	3072.13	1155.81	2059.92	1161.43
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	*P*-1	*P*-1	$P2_1/n$	*P*-1	$P2_1/n$
a/Å	13.465(7)	13.714(3)	10.6926(13)	12.134(2)	10.616(2)
b/Å	14.582(8)	15.294(3)	22.839(3)	17.393(3)	40.964(9)
c/Å	15.016(8)	16.424(3)	24.066(3)	27.747(5)	13.602(3)
α/°	68.274(9)	78.172(4)	90.00	85.016(4)	90.00
β/°	70.498(8)	81.154(4)	98.332(2)	79.956(4)	96.722(4)
γ/°	74.301(9)	80.768(4)	90.00	73.461(4)	90.00
U/Å^3	2545(2)	3301.8(12)	5814.9(12)	5523.4(18)	5874(2)
Z	2	1	4	2	4
M(Mo-Kα)/mm^{-1}	0.128	1.366	0.807	0.487	0.756
Total reflections	29347	38813	51983	43509	47088
Unique reflections	11659	15311	13990	14545	11990
R_{int}	0.0271	0.0328	0.0546	0.1114	0.0615
R_1 (all data)	0.0905	0.101	0.0989	0.1491	0.0837
R_1 ($I_o > 2\sigma(I_o)$)	0.0637	0.0737	0.0656	0.0890	0.0529
wR_2 ($I_o > 2\sigma(I_o)$)	0.1522	0.221	0.1167	0.1796	0.1193
2θ max/°	28.1	28.02	27.98	22.56	26.37
*wR*2 (all data)	0.1662	0.2411	0.1265	0.2050	0.1305

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complex (**3**) could be located. Hydrogen atoms attached to the allyl carbon atoms in complex (**2**) were not fixed owing to disorder (manifested in the large anisotropic temperature factors of these atoms). The oxygen atom O(6) of the water molecule coordinated to Pd(4) and the acetone molecule present in the lattice of (**2**) have been assigned a partial occupancy factor of 0.5. The oxygen atom O(6) is at a distance of 1.89 Å from the acetone carbon atom C(57). A summary of the crystallographic data for complexes (**2**), (**3**), (**4**), (**6**) and (**L′**) is given in Table 4.

CCDC reference numbers 637406 (**2**), 637407 (**3**), 637408 (**4**), 618420 (**6**) and 637409 (**L′**).

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b703308g

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