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Steric and electronic effects in stabilizing allyl-palladium complexes of "P–N–P" ligands, $X_2PN(Me)PX_2$ ($X = OC_6H_5$ or $OC_6H_3Me_2$-2,6) ☆

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Abstract

The chemistry of η^3-allyl palladium complexes of the diphosphazane ligands, $X_2PN(Me)PX_2$ [$X = OC_6H_5$ (**1**) or $OC_6H_3Me_2$-2,6 (**2**)] has been investigated. The reactions of the phenoxy derivative, $(PhO)_2PN(Me)P(OPh)_2$ with $[Pd(\eta^3\text{-}1,3\text{-}R',R''\text{-}C_3H_3)(\mu\text{-}Cl)]_2$ ($R' = R'' = H$ or Me; $R' = H$, $R'' = Me$) give exclusively the palladium dimer, $[Pd_2\{\mu\text{-}(PhO)_2PN(Me)P(OPh)_2\}_2Cl_2]$ (**3**); however, the analogous reaction with $[Pd(\eta^3\text{-}1,3\text{-}R',R''\text{-}C_3H_3)(\mu\text{-}Cl)]_2$ ($R' = R'' = Ph$) gives the palladium dimer and the allyl palladium complex $[Pd(\eta^3\text{-}1,3\text{-}R',R''\text{-}C_3H_3)(\mathbf{1})](PF_6)$ ($R' = R'' = Ph$) (**4**). On the other hand, the 2,6-dimethylphenoxy substituted derivative **2** reacts with (allyl) palladium chloro dimers to give stable allyl palladium complexes, $[Pd(\eta^3\text{-}1,3\text{-}R',R''\text{-}C_3H_3)(\mathbf{2})](PF_6)$ [$R' = R'' = H$ (**5**), Me (**7**) or Ph (**8**); $R' = H$, $R'' = Me$ (**6**)]. Detailed NMR studies reveal that the complexes **6** and **7** exist as a mixture of isomers in solution; the relatively less favourable isomer, *anti*-$[Pd(\eta^3\text{-}1\text{-}Me\text{-}C_3H_4)(\mathbf{2})](PF_6)$ (**6b**) and *syn*/*anti*-$[Pd(\eta^3\text{-}1,3\text{-}Me_2\text{-}C_3H_3)(\mathbf{2})](PF_6)$ (**7b**) are present to the extent of 25% and 40%, respectively. This result can be explained on the basis of the steric congestion around the donor phosphorus atoms in **2**. The structures of four complexes (**4**, **5**, **7a** and **8**) have been determined by X-ray crystallography; only one isomer is observed in the solid state in each case.

Keywords: Allyl complexes; P ligands; Diphosphazanes; NMR spectroscopy; Palladium; X-ray crystallography

1. Introduction

Palladium catalysed allylic substitution reactions constitute a powerful methodology for C–C bond formation in organic synthesis [1]. The configuration of the final product strongly depends on the configuration of an intermediate of the type $[Pd(\eta^3\text{-allyl})(\text{auxillary ligand})]^+$ and its rigidity in solution [2]. The catalytic conversion of (*E*)-allyl substrate to (*E*)-allyl product is a straightforward process that proceeds via the more favourable *syn*-configured allyl palladium intermediate (Scheme 1). On the other hand, the less favourable *anti*-configured allyl palladium complex is generated by the attack of palladium catalyst on the (*Z*)-allyl substrate which should subsequently lead to the formation of (*Z*)-allyl product provided that no η^3–η^1–η^3 isomerization occurs at all or the rate of the isomerization is slower than the nucleophilic attack. However, in reality the *anti*-allyl palladium complexes undergo a fast η^3–η^1–η^3 isomerization to the more favourable *syn*-allyl palladium isomers that leads to (*E*)-allyl product by subsequent nucleophilic attack. Thus, the η^3–η^1–η^3 isomerization step actually determines whether a given (*Z*)-allyl substrate will lead to retention of configuration or not in the final product. One way of controlling the η^3–η^1–η^3 isomerization step is to introduce a sterically bulky substituent in the auxillary ligand so that the less favourable *anti*-allyl palladium isomer would be stabilised [3]. Such a possibility has been realised with phenyl substituted allyl palladium complexes

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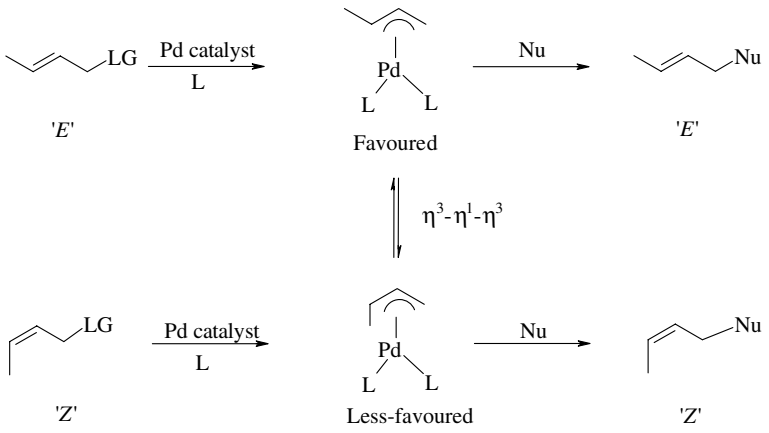

Scheme 1.

which adopt the less favourable *syn*/*anti* or *anti*/*anti* configuration characterised both in solid state [4] and in solution [5a]. However the situation becomes more challenging when the allyl moiety carries relatively small methyl groups [3].

As a part of our ongoing investigations on the organometallic chemistry of diphosphazane ligands, [6,7] we reported the synthesis and dynamic behaviour of allyl palladium complexes of a range of diphosphazane and diphosphazane monosulfide ligands [7]. Diphosphazanes constitute a class of versatile short-bite bidentate phosphorus-donor ligands based on the "P–N–P" framework that have engendered a varied and extensive transition metal organometallic chemistry [8]. The allyl palladium complexes of diphosphonite ligands are rare in literature and this is probably attributed to the higher π-acidity of these ligands owing to the presence of two electronegative oxygen atoms attached to the phosphorus centre as compared to the diphosphane ligands. A recent study by Calabrò et al. [5a] shows that the optically pure diphosphazane diphosphonite ligand $(C_{20}H_{12}O_2)PN(R)P(C_{20}H_{12}O_2)$ (R = Ph or (*S*)-*sec*-butyl) effectively forms the palladium allyl complex characterized by NMR study in solution although no solid-state structure of any such complexes were reported. (Allyl) palladium complexes of a diphosphazane monoxide viz. $Ph_2PNHP(O)Ph_2$ have been reported by Woollins and coworkers [5b]. In this paper, we report the reactions of various allyl-palladium dimers, $[Pd(\eta^3\text{-}1,3\text{-}R',R''\text{-}C_3H_3)(\mu\text{-}Cl)]_2$ with symmetrically substituted diphosphazane diphosphonite ligands, $X_2PN(Me)PX_2$ [X = OC_6H_5 (**1**) or $OC_6H_3Me_2$-2,6 (**2**)]. The products have been characterised by NMR spectroscopy and X-ray crystallography.

2. Experimental

All reactions and manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk and vacuum-line techniques. The solvents were purified by standard procedures [9] and distilled under nitrogen prior to use. The chlorobridged palladium allyl dimers, $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ [10], $[Pd(\eta^3\text{-}Me\text{-}C_3H_4)(\mu\text{-}Cl)]_2$, $[Pd(\eta^3\text{-}1,3\text{-}Me_2\text{-}C_3H_3)(\mu\text{-}Cl)]_2$ [11] and $[Pd(\eta^3\text{-}1,3\text{-}Ph_2\text{-}C_3H_3)(\mu\text{-}Cl)]_2$ [12] were prepared as previously described. The diphosphazane ligand **1** [13a] and **2** [13b] were prepared by analogous procedures. The NMR spectra were recorded using Bruker DRX-500 MHz, Bruker AMX-400 MHz and Bruker ACF-200 MHz spectrometers. Chemical shifts downfield from the reference standard were assigned positive values. Elemental analyses were carried out using a Perkin–Elmer 2400 CHN analyser.

2.1. Synthesis of palladium complexes

2.1.1. $[Pd(\eta^3\text{-}1,3\text{-}Ph_2\text{-}C_3H_3)\{\kappa^2\text{-}(PhO)_2PN(Me)\text{-}P(OPh)_2\}](PF_6)$ (**4**)

A mixture of $[Pd(\eta^3\text{-}1,3\text{-}Ph_2\text{-}C_3H_3)(\mu\text{-}Cl)]_2$ (0.067 g, 0.99×10^{-4} mol), NH_4PF_6 (0.033 g, 2.02×10^{-4} mol) and ligand **1** (0.095 g, 2.05×10^{-4} mol) were dissolved in 20 cm^3 of acetone. The solution was stirred for 1 h at 298 K and the white precipitate formed during the reaction was filtered off. The resulting yellow orange filtrate was concentrated under reduced pressure to 10 cm^3 and the solution was layered by adding 10 cm^3 of hexane (b.p. 40–60 °C) to yield yellow crystals. The compound was purified by crystallization from acetone–hexane (1:1 v/v). The other allyl palladium complexes **5**–**8** were synthesised by an analogous procedure by varying the allyl palladium chloro dimer and the diphosphazane ligand. The yields, melting points and elemental analyses for these complexes are given in Table 5. Selected ^1H, $^{31}P\{^1H\}$ and ^{13}C NMR spectral values for complexes **4**–**8** are given in Table 1.

3. X-ray crystallography

The crystals were mounted on a glass fibre and the intensity data for all the complexes were obtained at room temperature from a Bruker SMART APEX CCD diffractometer equipped with fine focus 1.75 kW sealed tube Mo Kα X-ray source with increasing ω (width of 0.3° per frame) at a scan speed of *n* s/frame ($n = 15$ for **4**, $n = 10$ for **6a**, $n = 9$ for **7a** and $n = 15$ for **8**).