Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Organometallic Chemistry 691 (2006) 2969–2977
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

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) ☆

Swadhin K. Mandal, Thengarai S. Venkatakrishnan, Arindam Sarkar, Setharampattu S. Krishnamurthy *

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, India

Received 7 February 2006; received in revised form 28 February 2006; accepted 28 February 2006
Available online 6 March 2006

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

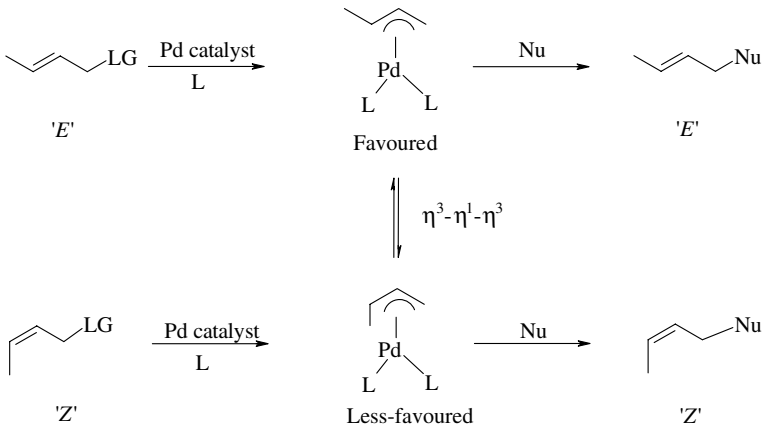
1. Introduction

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

☆ Part 25 of the series "Organometallic Chemistry of diphosphazanes"; for Part 24, see [6c].

* Corresponding author. Tel.: +91 80 22932401; fax: +91 80 23600683/23601552.
E-mail address: sskrish@ipc.iisc.ernet.in (S.S. Krishnamurthy).

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.02.040



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**).

Table 1
Selected ^{1}H, $^{31}P\{^{1}H\}$ and ^{13}C NMR spectral values for complexes **4–8** (only allyl protons and carbon nuclei are listed)

Complex	$^{31}P\{^{1}H\}$[a] NMR	^{1}H NMR[b]					^{13}C NMR[b]		
		H_s	H_a	H'_s	H'_a	H_c	C_t	C'_t	C_c
4	108.1 s	–	–	–	5.65 m	6.23 t	–	93.1 t (24.1)	112.6 t (9.1)
5	109.1 s	4.32 m	2.69 m	–	–	4.92 m	75.3 br.d (52.2)[f]	–	124.7 t (14.7)
6a	108.8 d and 110.7 d (13.0)[c]	4.01 m	2.41 t (13.5)[d,e]	–	3.77 m	4.95 m	68.2 dd (40.3)[f] (13.7)[g]	101.9 dd (40.8)[f] (12.6)[g]	123.5 t (12.9)
6b	107.3 d and 111.7 d (4.4)[c]	3.74 m	2.94 t (15.7)[d,e]	5.47 m	–	4.61 m	67.3 dd (42.5)[f] (11.6)[g]	98.2 dd (37.0)[f] (10.3)[g]	118.4 t (12.7)
7a	110.9 s	–	–	–	3.52 m	5.13 t (11.2)[d]	–	93.8 t (24.8)[f]	124.1 t (13.9)
7b	111.6 d and 110.3 d (35.7)[c]	–	–	5.19 m	4.08 m	4.78 br.t	–	92.3 dd (40.9)[f] (12.5)[g] and 90.4 dd (36.9)[f] (12.3)[g]	119.3 t (13.8)
8	108.5 s	–	–		5.13 m	6.11 m			

Abbreviations: d, doublet; br.d, broad doublet; dd, doublets of doublet; t, triplet; br.t, broad triplet; m, multiplet.
Coupling constants in Hz are given in parenthesis. H_s and H_a are the *syn* and *anti* allylic protons at the unsubstituted allyl terminus, respectively. H'_s and H'_a are the *syn* and *anti* allylic protons at the substituted allyl terminus, respectively. H_c is the central allyl proton. C_t is unsubstituted terminal allyl carbon. C'_t is substituted terminal allyl carbon. C_c is central allyl carbon.
[a] Acetone was used as solvent.
[b] $CDCl_3$ was used as solvent.
[c] J(P,P).
[d] J(H,H).
[e] J(P,H).
[f] $^{2}J(P,C)_{trans}$.
[g] $^{2}J(P,C)_{cis}$.

Details of crystallographic data collection are summarised in Table 2. The SMART [14a] software was used for cell-refinement and data acquisition and the SAINT [14b] software was used for data reduction. Lorentzian and polarization corrections were made on the intensity data. An absorption correction was made on the intensity data using the SADABS [14c] program. All the structures were solved using SHELXTL [14d] and the WINGX graphical user interface [15]. Least-square refinements were performed by the full-matrix method with SHELXL-97 [16]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically.

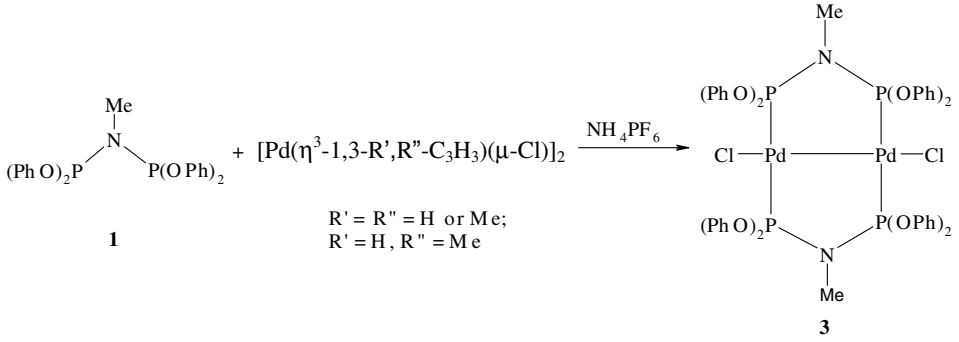
Table 2
Details of X-ray crystallographic data collection for the complexes **4** and **7a**

Complex	**4**	**7a**
Empirical formula	$C_{40}H_{36}NO_4F_6P_3Pd$	$C_{38}H_{48}NO_4F_6P_3Pd$
Formula weight	908.01	896.08
Colour	Yellow	Light yellow
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$
a (Å)	10.243(1)	9.818(7)
b (Å)	15.601(2)	21.389(15)
c (Å)	24.886(3)	19.731(14)
α (°)	90.000	90.000
β (°)	95.721(2)	94.969(12)
γ (°)	90.000	90.000
V (Å^3)	3956.7(9)	4128(5)
Z	4	4
Density (calcd) (Mg/mm^3)	1.524	1.442
Absorption coefficient (mm^{-1})	0.660	0.631
F(000)	1840	1840
Crystal size (mm)	$0.275 \times 0.159 \times 0.102$	$0.75 \times 0.44 \times 0.18$
θ Range (°)	1.54–27.5	1.90–27.7
Index range	$-13 \leqslant h \leqslant 13$, $-20 \leqslant k \leqslant 20$, $-32 \leqslant l \leqslant 28$	$-12 \leqslant h \leqslant 11$, $-28 \leqslant k \leqslant 28$, $-26 \leqslant l \leqslant 25$
Reflections collected	34226	35871
Independent reflections [R_{int}]	9338 [0.0458]	9708 [0.0414]
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/restraints/parameters	9338/0/496	9708/0/478
Goodness of fit on F^2	0.799	1.030
Final R indices ($I > 2\sigma_I$)	$R_1 = 0.0424$, $wR_2 = 0.1172$	$R_1 = 0.0514$, $wR_2 = 0.1433$
R indices (all data)	$R_1 = 0.0655$, $wR_2 = 0.1305$	$R_1 = 0.0703$, $wR_2 = 0.1542$
Largest differential peak and hole (e Å^{-3})	0.609 and −0.505	1.186 and −0.557

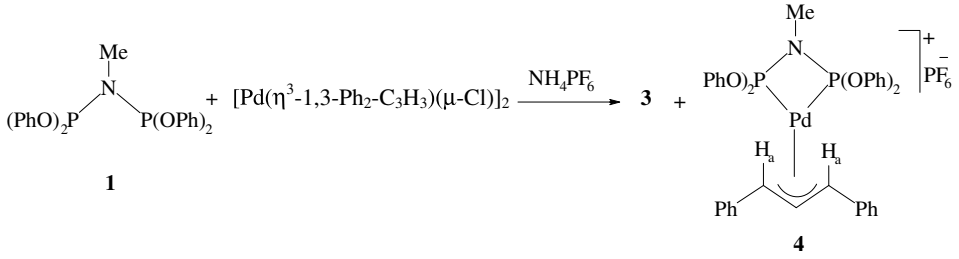
4. Results and discussion

4.1. Reactions of $X_2PN(Me)PX_2$ [X = OC_6H_5 (1)] with [Pd(η^3-1,3-R′,R″-C_3H_3)(μ-Cl)]$_2$

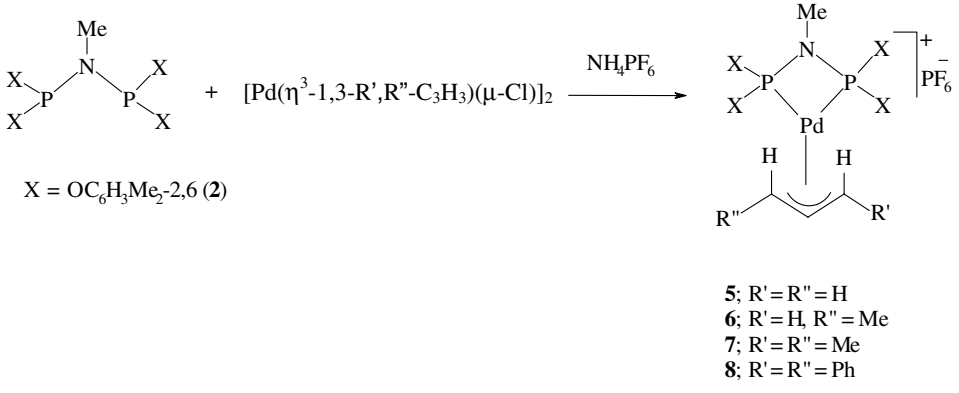
The reactions of $(PhO)_2PN(Me)P(OPh)_2$ with the [Pd(η^3-1,3-R′,R″-C_3H_3)(μ-Cl)]$_2$ (R′ = R″ = H or Me; R′ = H, R″ = Me) in the presence of NH_4PF_6 gives exclusively the known palladium chloro-dimer [17], [Pd_2{μ-P,P-$(PhO)_2$-PN(Me)P$(OPh)_2$}$_2Cl_2$] (**3**) in which the palladium center is reduced to the mono-valent oxidation state as shown in Scheme 2. The formation of the palladium dimer **3** is confirmed by its characteristic $^{31}P\{^1H\}$ NMR spectrum (singlet at 113.4 ppm) as well as by its ^1H and IR spectra. The di-palladium complex **3** has been synthesized previously by two other methods. The first method of synthesis involves a disproportionation reaction between a palladium(0) and a palladium(II) precursor [17]. The second method of synthesis consists of treatment of $(PhO)_2PN(Me)P(OPh)_2$ with a palladium(II) complex, [$PdCl_2$(COD)] [6d]. The absence of any palladium allyl complex in the reaction depicted in Scheme 2 is probably related to the nature of the phosphorus ligand, $(PhO)_2PN(Me)P(OPh)_2$. The two phosphonite phosphorus atoms in this ligand have a high π-acceptor capability which would destabilize palladium-allyl π-bonding. This inference is borne out by the reaction of the same ligand, $(PhO)_2PN(Me)P(OPh)_2$ with 1,3-diphenyl-allyl-dimer in the presence of NH_4PF_6, in which the major product is the palladium-allyl-diphosphazane complex **4** (Scheme 3). The chloro palladium dimer **3** is also formed in this reaction as shown by the ^{31}P NMR spectrum of the reaction mixture. The allyl complex **4** is characterized by ^1H, $^{31}P\{^1H\}$ and ^{13}C NMR spectra (see Table 1) and single crystal X-ray crystallography. The formation of the allyl complex **4** only in the case of 1,3-diphenyl-allyl precursor suggests that the presence of the two electron-releasing phenyl groups enhances



Scheme 2.



Scheme 3.



Scheme 4.

the π-donor character of the allyl moiety and in turn enables effective π-back donation from the metal to the diphosphazane ligand. Previously we had reported a similar electronic effect in the allyl palladium complexes of the diphosphazane ligand, $Ph_2PN(CHMe_2)PPh(N_2C_3HMe_2$-3,5) which exhibits ambident coordination behaviour (P,P- or P,N-mode) only in the case of 1,3-diphenyl-allyl complex [7b].

4.2. Reactions of $X_2PN(Me)PX_2$, $X = OC_6H_3Me_2$-2,6 (2) with $[Pd(\eta^3$-1,3-R′,R″-$C_3H_3)(\mu$-Cl)$]_2$

The incorporation of two methyl groups at the 2- and 6-positions of the phenyl rings in the ligand $(PhO)_2PN(Me)$-$P(OPh)_2$ can have two effects. The first one is that it can enhance the electron donating capacity of the two phosphorus atoms owing to the inductive effect of the methyl groups on the phenyl rings. Secondly, the methyl groups at the 2- and 6-positions of the phenyl rings would provide steric crowding around the donating phosphorus centres. The reactions of $X_2PN(Me)PX_2$ ($X = OC_6H_3Me_2$-2,6) with $[Pd(\eta^3$-1,3-R′,R″-$C_3H_3)(\mu$-Cl$)]_2$ (R′ = R″ = H, Me or Ph; R′ = H or R″ = Me) in the presence of NH_4PF_6 yield the allyl complexes **5**–**8** as shown in Scheme 4. The $^{31}P\{^1H\}$

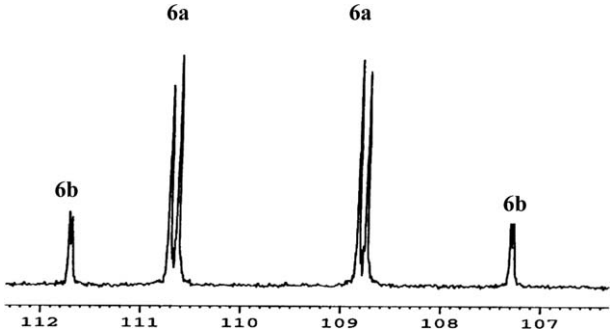
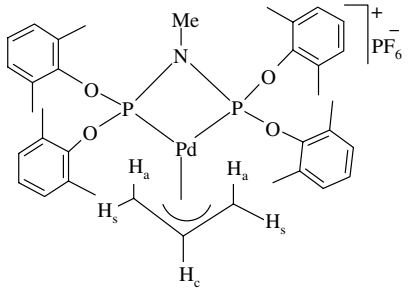
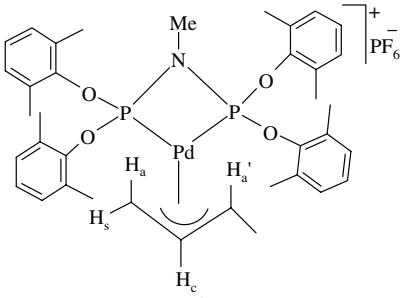


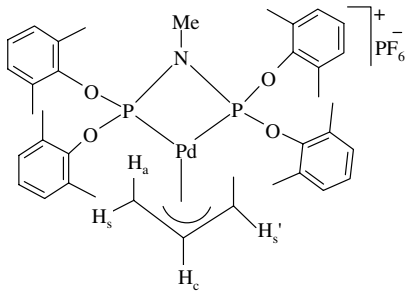
Fig. 1. The $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) spectrum of $[Pd(\eta^3$-Me-$C_3H_4)\{\kappa^2$-$X_2PN(Me)PX_2\}](PF_6)$ [$X = OC_6H_3Me_2$-2,6 (**6**)] revealing two isomers in solution.



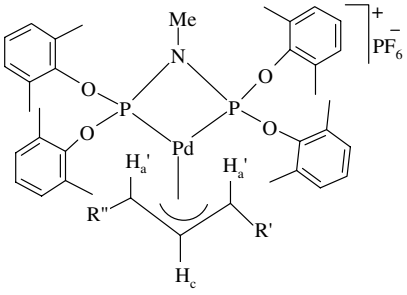
5



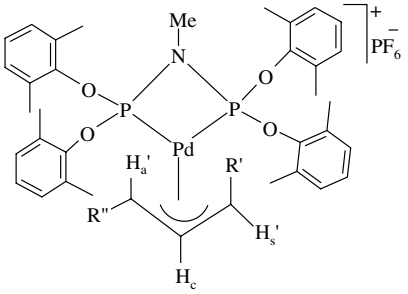
Syn-, **6a**



Anti-, **6b**



Syn/syn-, **7a**; R' = R" = Me
Syn/syn-, **8**; R' = R" = Ph



Syn/anti-, **7b**; R' = R" = Me

Fig. 2. The allyl complexes, $[Pd(\eta^3$-1,3-R′-R″-$C_3H_3)\{\kappa^2$-P,P-$X_2PN(Me)PX_2\}](PF_6)$ (**5**–**8**) of the diphosphazane ligand $X_2PN(Me)PX_2$ ($X = OC_6H_3Me_2$-2,6).

NMR spectrum of the reaction mixture shows the exclusive formation of allyl complexes in each of these reactions and a palladium dimer of the type **3** is not formed. The complexes **5**–**8** are characterized by NMR spectroscopy and elemental analyses. The $^{31}P\{^1H\}$ NMR spectra of **6** (Fig. 1) and **7** show the presence of two isomers (see Table 1). The ^{31}P chemical shifts for the allyl complexes **4**–**8** lie upfield compared to those of the ligands **1** and **2** (δp 135.5 and 134.9, respectively). This trend is reverse of that observed for the (η^3-allyl) palladium complexes of the "P–N–P" ligands, $Ph_2PN(R)PPh_2$ [7c].

The ^1H and ^{13}C NMR spectral data for **5**–**8** are presented in Table 1. The ^1H–^1H COSY and NOESY spectra suggest that the major isomer **6a** contains a *syn* allyl-methyl group with respect to the central allyl proton whereas the minor isomer **6b** possesses an *anti* arrangement of the allyl-methyl group (see Fig. 2). The $^{31}P\{^1H\}$ NMR spectrum of the 1,3-dimethyl-allyl complex, $[Pd(\eta^3\text{-}1,3\text{-}Me_2\text{-}C_3H_3)\{\kappa^2\text{-}P,P\text{-}X_2PN(Me)PX_2\}](PF_6)$ ($X = OC_6H_3Me_2$-2,6) (**7**) reveals that complex **7** exists as a mixture of two isomers; the spectrum displays a singlet and two doublets (AB pattern) in the ratio 1.4:1.0. The observed AB pattern in the $^{31}P\{^1H\}$ spectrum for the minor isomer indicates that the two palladium bound allyl termini are no longer equivalent to each other. On the basis of a detailed NMR investigation (^1H–^1H NOESY, ^1H–^1H ROESY and ^1H–^1H COSY) the major isomer is assigned the *syn*/*syn*-configuration while the minor isomer is assigned the *syn*/*anti*-configuration as shown in Fig. 2. The ^1H–^1H NOESY spectrum (Fig. 3) clearly points to the *syn*/*anti*-configuration for the minor isomer **7b**. The *anti*-allyl-methyl protons centred at 0.50 ppm shows a strong NOE cross-peak to the *anti*-allyl proton (H_a') at 4.08 ppm but does not show any NOE cross-peak to the central allyl proton H_c at 4.78 ppm. Both **6** and **7** do not show any dynamic behaviour at 298 K as revealed by their phase sensitive ^1H–^1H NOESY and ROESY spectra; presumably the inter-conversion is slow on the NMR time scale at this temperature.

The less favourable *anti*-isomer **6b** and the *syn*/*anti*-isomer **7b** are observed in solution to the extent of 25% and 40%, respectively, as revealed by their $^{31}P\{^1H\}$ and ^1H NMR spectra. These are the highest relative abundances of less favourable isomers observed in solution for any palladium methyl-substituted-allyl complexes bearing the diphosphazane ligands [5,7]. This result may be attributed to the increasing steric demand of the 2- and 6-methyl groups on the phenyl rings which would interact with the *syn* allyl-methyl group forcing the *syn*-isomer to adopt an *anti*-configuration to a relatively larger extent. It is reported that the allyl-palladium complexes tend to adopt a *syn*-configuration and the less stable *anti*-isomer is generally present in less than 10% relative abundance except in some special cases [18]. Exceptions arise when the steric interactions either between the allyl moiety and the ligand or between the substituents on the allyl moiety destabilize the *syn*-isomer [3,18,19]. The formation of the *anti*-isomer is also significant from the point of view of obtaining a

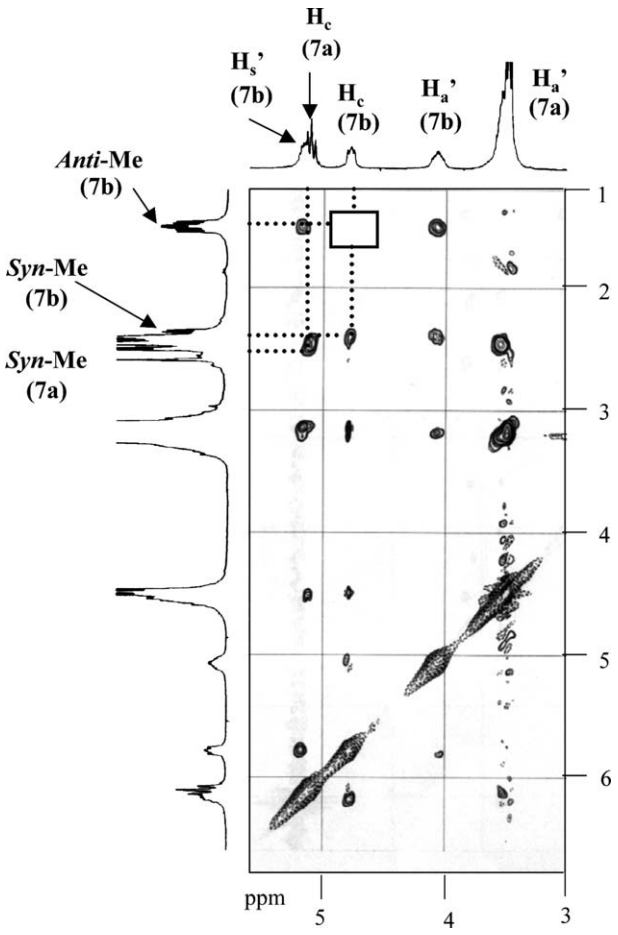


Fig. 3. The ^1H–^1H NOESY (400 MHz, $CDCl_3$) spectrum of $[Pd(\eta^3\text{-}1,3\text{-}Me_2\text{-}C_3H_3)\{\kappa^2\text{-}P,P\text{-}X_2PN(Me)PX_2\}](PF_6)$ [$X = OC_6H_3Me_2$-2,6 (**7**)] revealing the minor isomer (**7b**) as a *syn*/*anti*-isomer. Empty box indicates the absence of any NOE cross-peak between *anti*-allyl-methyl protons and H_c in the minor isomer, **7b**.

Z-configured product after reaction with a nucleophile irrespective of the configuration of the starting material provided no π–σ–π isomerization occurs (see Scheme 1) [20]. Generally, in the palladium-promoted catalytic reactions, the *E*-configured products are obtained and selective conversion of (*Z*)-allyl substrate with retention of the olefin geometry remains as one of the most difficult problems to solve [21]. The reaction of **2** with $[Pd(\eta^3\text{-}1,3\text{-}Ph_2\text{-}C_3H_3)(\mu\text{-}Cl)]_2$ gives an orange colour product as the major component, which is insoluble in common organic solvents and could not be characterized, and a *syn*/*syn*-1,3-diphenyl-allyl complex $[Pd(\eta^3\text{-}1,3\text{-}Ph_2\text{-}C_3H_3)\{\kappa^2\text{-}P,P\text{-}X_2PN(Me)PX_2\}](PF_6)$ (**8**, $X = OC_6H_3Me_2$-2,6) in less than 10% yield. The structure of **8** has been determined by X-ray crystallography (see below).

5. Solid state structures of 4, 5, 7a and 8

The molecular structure of **4**, **5**, **7a** and **8** has been determined by X-ray crystallography. The complexes are isostructural to each other and show similar trends in their

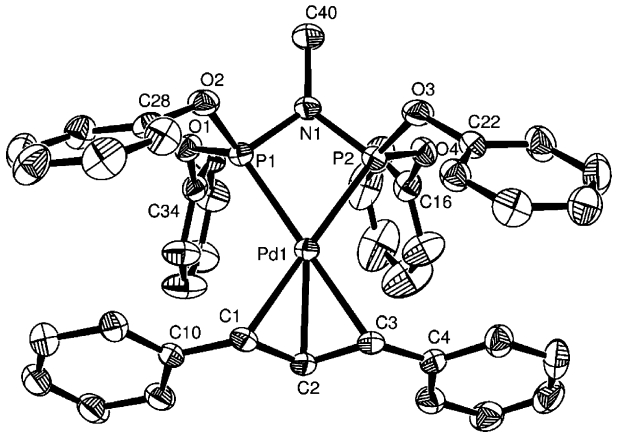


Fig. 4. The molecular structure of $[Pd(\eta^3\text{-}1,3\text{-}Ph_2\text{-}C_3H_3)\{\kappa^2\text{-}(PhO)_2PN(Me)P(OPh)_2\}]$ (**4**) in the solid state; hexafluorophosphate and hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability level.

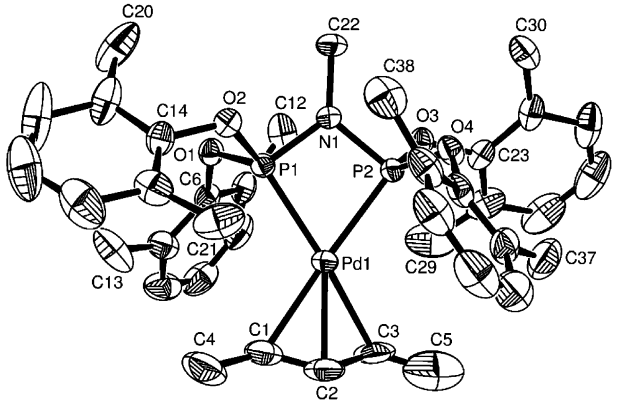


Fig. 5. The molecular structure of $[Pd(\eta^3\text{-}1,3\text{-}Me_2\text{-}C_3H_3)\{\kappa^2\text{-}X_2PN(Me)PX_2\}](PF_6)$ [$X = OC_6H_3Me_2$-2,6 (**7**)] revealing only one isomer **7a** in the solid state; hexafluorophosphate and hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability level.

structural parameters. For a comparison of the structural features of these complexes, selected data of **4** and **7a** only are included here. The data for the complexes **5** and **8** are given in the Supplementary material. The molecular structures of **4** and **7a** are shown in Figs. 4 and 5, respectively.

Table 3
Selected bond distances and angles for **4** and **7a**

	Complex **4**	Complex **7a**
Bond distances (Å)		
Pd(1)–C(1)	2.230(3)	2.211(6)
Pd(1)–C(2)	2.205(3)	2.169(4)
Pd(1)–C(3)	2.220(3)	2.172(6)
Pd(1)–P(1)	2.301(1)	2.296(1)
Pd(1)–P(2)	2.287(1)	2.315(2)
P(1)–N(1)	1.663(3)	1.666(3)
P(2)–N(1)	1.676(3)	1.675(3)
Bond angles (°)		
P(1)–Pd(1)–P(2)	69.42(3)	70.00(4)
C(1)–Pd(1)–C(3)	66.28(11)	65.7(2)
C(1)–Pd(1)–P(1)	112.22(9)	112.32(16)
C(1)–Pd(1)–P(2)	171.13(8)	176.5(3)
C(3)–Pd(1)–P(1)	175.59(9)	169.9(4)
C(3)–Pd(1)–P(2)	111.39(8)	112.55(18)
P(1)–N(1)–P(2)	102.96(14)	104.68(15)
O(1)–P(1)–O(2)	98.34(12)	99.87(12)
O(3)–P(2)–O(4)	98.48(14)	100.22(12)

Selected structural parameters of complexes **4** and **7a** are listed in Table 3.

The solid state structures of complexes **4**, **5**, **7a** and **8** reveal a distorted square planar geometry around the palladium. The distances and dihedral angles between the allyl moiety and mean plane formed by P(1), P(2) and Pd(1) are listed in Table 4. The plane of the allyl ligand is tilted from an axis perpendicular to the P–Pd–P coordination plane from its idealised position [ideally the dihedral angle between the allyl moiety and the coordination plane formed by P(1), Pd(1) and P(2) should be 90°]. Interestingly, the maximum deviation (48.2°) from the ideal value is observed for **7a** in which case the maximum population (40%) of the relatively less favourable *syn*/*anti*-isomer (**7b**) is observed in solution. The conversion of the *syn*/*syn*-isomer **7a** observed in the solid state into a mixture of **7a** and **7b** upon dissolution in chloroform can be explained by considering the well-known η^3–η^1–η^3 isomerization process in solution observed for other related palladium allyl complexes bearing diphosphazane ligands [7]. The bonding parameters fall in the expected ranges [7,22,23]. In complex **8** (see Supplementary material) the two Pd–P and Pd–C (terminal) bond lengths [Pd(1)–P(1) = 2.381(1) Å, Pd(1)–P(2) = 2.267(1) Å, Pd(1)–C(1) =

Table 4
The distances (Å) and dihedral angles (°) between the allyl moiety and mean plane formed by P(1), P(2) and Pd(1)

Compound	Distances[a] (Å) of terminal allyl carbon atoms		Distance[a] (Å) of central allyl carbon atom	Dihedral angle[b]
	C(1)	C(3)		
4	−0.34	−0.17	0.355	61.6 (28.4)
5	0.07	0.03	0.624	67.9 (22.1)
7a	0.10	−0.36	0.144	41.8 (48.2)
8	−0.24	−0.35	0.32	63.4 (26.6)

[a] The distances are from the mean plane formed by P(1), P(2) and Pd(1). Negative sign indicates the atom is located below the mean plane and the positive sign indicates the atom is located above the plane.

[b] Angle between the allyl plane and the mean plane formed by P(1), P(2) and Pd(1) atoms and the deviation from idealized values are in the parentheses.

Table 5
Yield, melting point and elemental analysis data for η^3-allyl palladium complexes **4–8**

Compound	Yield (%)	m.p. (°C)	Elemental analysis[a]		
			%C	%H	%N
4	50	152–155 (dec)	52.92 (52.78)	4.01 (3.96)	1.67 (1.54)
5	76	169–172 (dec)	49.58 (49.82)	5.16 (5.07)	1.46 (1.61)
6	79	163–165 (dec)	50.34 (50.39)	5.08 (5.22)	1.69 (1.58)
7	72	150–153 (dec)	50.84 (50.94)	5.37 (5.36)	1.60 (1.56)
8	50	200–202 (dec)	56.50 (56.69)	5.14 (4.98)	1.37 (1.27)

[a] Calculated values are in parentheses.

2.183(4) Å (*trans* to P(1)), Pd(1)–C(3) = 2.337(4) Å (*trans* to P(2))] differ significantly. Probably the crowding between 1,3-diphenyl allyl moiety and the methyl groups of ligand **2** in complex **8** forces the allyl moiety to bind unsymmetrically with the Pd centre. A similar type of bond distortion originating purely from steric constraints was observed previously in the case of 1,3-diphenyl-allyl complex of a symmetrically substituted P-stereogenic ligand, 1,1′-bis(naphthylphenylphosphino)ferrocene [22a].

6. Conclusion

The interplay of steric and electronic effects is evident in the reactions of 'P–N–P' ligands of the type $X_2PN(Me)PX_2$ with (allyl) chloro palladium dimers. The formation of the chloro palladium(I) dimer $[ClPd(\mu\text{-}X_2PN(Me)PX_2)]_2$ and the absence of a (allyl) palladium complex in the reaction of $[Pd(\eta^3\text{-}1,3\text{-}R', R''\text{-}C_3H_3)(\mu\text{-}Cl)]_2$ ($R' = R'' = H$ or Me; $R' = H$, $R'' = Me$) with $X_2PN(Me)PX_2$ ($X = OPh$) ligand indicates that this ligand bearing two phosphonite phosphorus atoms behaves as a strong π-acceptor and destabilizes metal to allyl π-interactions. A moderately stable allyl complex could be obtained when electron releasing phenyl groups are introduced in the allyl moiety. On the other hand, when the σ-donor ability of the auxiliary ligand is increased by incorporating eight methyl groups at the 2- and 6-positions of the aryl rings of the ligand $X_2PN(Me)PX_2$ ($X = OC_6H_3Me_2$-2,6), (allyl) palladium complexes are the only products. At the same time, the methyl groups at 2- and 6-positions of the aryl rings of the ligand $X_2PN(Me)PX_2$ ($X = OC_6H_3Me_2$-2,6) exert a significant steric effect in determining the relative abundance of two isomers of (allyl) palladium complexes **6** and **7**. The isomers with less favourable allylic arrangements *anti* (**6b**) and *syn*/*anti* (**7b**) are formed in exceptionally high amounts as compared to the other allyl complexes of diphosphazane ligands.

7. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. 295738 (**4**), 295739 (**5**), 295740 (**7a**) and 295741 (**8**). Copies of the data can be obtained free of charge from the Director, CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the Department of Science and Technology (DST), New Delhi, India for financial support and CCD X-ray facility at IISc Bangalore set up under IRHPA programme. We thank NMR research center (formerly Sophisticated Instruments Facility), IISc, Bangalore for NMR measurements. SSK thanks Indian National Science Academy, New Delhi for the position of a Senior Scientist.

References

[1] (a) B.M. Trost, T.R. Verhoeven, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 8, Pergamon Press, Oxford, 1982, pp. 799–938;
(b) B.M. Trost, D.L.V. Vranken, Chem. Rev. 96 (1996) 395–422;
(c) B.M. Trost, M.L. Crawley, Chem. Rev. 103 (2003) 2921–2943;
(d) P. von Matt, A. Pfaltz, Angew. Chem., Int. Ed. Engl. 32 (1993) 566–568;
(e) A. Pfaltz, M. Lautens, in: E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), Comprehensive Asymmetric Catalysis, Springer, Heidelberg, 1999, pp. 833–886;
(f) J. Helmchen, A. Pfaltz, Acc. Chem. Res. 33 (2000) 336–345;
(g) C.G. Frost, J. Howarth, J.M.J. Williams, Tetrahedron: Asymmetry 3 (1992) 1089–1122;
(h) G. Helmchen, J. Organomet. Chem. 576 (1999) 203–214.
[2] P.W.N.M. van Leeuwen, Homogeneous Catalysis: Understanding the Art, Kluwer Academic Publishers, Dordrecht, Netherlands, 2004, pp. 271–298.
[3] M. Sjögren, S. Hansson, P.-O. Norrby, B. Åkermark, M.E. Cucciolito, A. Vitagliano, Organometallics 11 (1992) 3954–3964.
[4] A. Togni, U. Burckhardt, V. Gramlich, P.S. Pregosin, R. Salzmann, J. Am. Chem. Soc. 118 (1996) 1031–1037.
[5] (a) G. Calabrò, D. Drommi, G. Bruno, F. Faraone, Dalton Trans. (2004) 81–89;
(b) A.M.Z. Slawin, M.B. Smith, J.D. Woollins, J. Chem. Soc., Dalton Trans. (1996) 1283–1293.
[6] (a) K. Raghuraman, S.K. Mandal, T.S. Venkatakrishnan, S.S. Krishnamurthy, M. Nethaji, Proc. Indian Acad. Sci. (Chem. Sci.) 114 (2002) 233–246;
(b) T.S. Venkatakrishnan, S.S. Krishnamurthy, M. Nethaji, J. Organomet. Chem. 690 (2005) 4001–4017;
(c) T.S. Venkatakrishnan, S.S. Krishnamurthy, M. Nethaji, J. Organomet. Chem. 691 (2006) 224–228;
(d) M. Ganesan, S.S. Krishnamurthy, M. Nethaji, J. Organomet. Chem. 690 (2005) 1080.
[7] (a) S.K. Mandal, G.A.N. Gowda, S.S. Krishnamurthy, C. Zheng, S. Li, N.S. Hosmane, Eur. J. Inorg. Chem. (2002) 2047–2056;

(b) S.K. Mandal, G.A.N. Gowda, S.S. Krishnamurthy, M. Nethaji, Dalton Trans. (2003) 1016–1027;
(c) S.K. Mandal, G.A.N. Gowda, S.S. Krishnamurthy, C. Zheng, S. Li, N.S. Hosmane, J. Organomet. Chem. 676 (2003) 22–37;
(d) S.K. Mandal, G.A.N. Gowda, T. Stey, D. Stalke, J. Organomet. Chem. 690 (2005) 742–750.

[8] (a) M.S. Balakrishna, V.S. Reddy, S.S. Krishnamurthy, J.F. Nixon, J.C.T.R. Burckett St. Laurent, Coord. Chem. Rev. 129 (1994) 1–90;
(b) M. Witt, H.W. Roesky, Chem. Rev. 94 (1994) 1163–1181;
(c) P. Bhattacharyya, J.D. Woollins, Polyhedron (1995) 3367–3388.

[9] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, third ed., Pergamon Press, Oxford, UK, 1988.

[10] Y. Tatsuno, T. Yoshida, S. Otsuka, Inorg. Synth. 28 (1990) 342–345.

[11] P.R. Auburn, P.B. MacKenzie, B. Bosnich, J. Am. Chem. Soc. 107 (1985) 2033–2046.

[12] P. von Matt, G.C. Lloyd-Jones, A.B.E. Minidis, A. Pfaltz, L. Macko, M. Neuburger, M. Zehnder, H. Rueegger, P.S. Pregosin, Helv. Chim. Acta 78 (1995) 265–284.

[13] (a) M.S. Balakrishna, T.K. Prakasha, S.S. Krishnamurthy, U. Siriwardane, N.S. Hosmane, J. Organomet. Chem. 390 (1990) 203–216;
(b) M. Raja, S.S. Krishnamurthy, unpublished results.

[14] (a) Bruker SMART, V. 6.028, Bruker AXS Inc., Madison, WI, USA, 1998;
(b) Bruker SAINT, V. 6.02, Bruker AXS Inc., Madison, WI, USA, 1998;
(c) G.M. Sheldrick, SADABS, University of Göttingen, Germany, 1997;
(d) Bruker SHELXTL, NT V. 5.10, Bruker AXS Inc., Madison, WI, USA, 1998.

[15] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837–838.

[16] G.M. Sheldrick, SHELXL-97, Program for refinement of crystal structures, University of Göttingen, Germany, 1997.

[17] M.S. Balakrishna, S.S. Krishnamurthy, R. Murugavel, I.I. Mathews, M. Nethaji, J. Chem. Soc., Dalton Trans. (1993) 477–482.

[18] B. Åkermark, S. Hansson, A. Vitagliano, J. Am. Chem. Soc. 112 (1990) 4587–4588.

[19] (a) J.W. Faller, M.E. Thomsen, M.J. Mattina, J. Am. Chem. Soc. 93 (1971) 2642–2653;
(b) J. Lukas, J.E. Ramakers-Blom, T.G. Hewitt, J.J. de Boer, J. Organomet. Chem. 46 (1972) 167–177.

[20] P. Corradini, G. Maglio, A. Musco, G. Paiaro, J. Chem. Soc., Chem. Commun. (1966) 618–619.

[21] (a) U. Kazmaier, F.L. Zumpe, Angew. Chem., Int. Ed. Engl. 39 (2000) 802–804;
(b) S.-K. Kang, S.-G. Kim, J.-S. Lee, Tetrahedron: Asymmetry 3 (1992) 1139–1140;
(c) T. Doi, A. Yanagisawa, M. Miyazawa, K. Yamamoto, Tetrahedron: Asymmetry 6 (1995) 389–392;
(d) B.M. Trost, M.A. Ceschi, B. König, Angew. Chem., Int. Ed. Engl. 36 (1997) 1486–1489.

[22] (a) U. Nettekoven, M. Widhalm, H. Kalchhauser, P.C.J. Kamer, P.W.N.M. van Leeuwen, M. Lutz, A.L. Spek, J. Org. Chem. 66 (2001) 759–770;
(b) D. Drago, P.S. Pregosin, J. Chem. Soc., Dalton Trans. (2000) 3191–3196;
(c) P.S. Pregosin, H. Rüegger, R. Salzmann, A. Albinati, F. Lianza, R.W. Kunz, Organometallics 13 (1994) 83–90.

[23] (a) T.G. Appleton, H.C. Clark, L.E. Manzer, Coord. Chem. Rev. 10 (1973) 335–422;
(b) J.W. Faller, N. Sarantopoulos, Organometallics 23 (2004) 2008–2014;
(c) J.-M. Camus, J. Andrieu, P. Richard, R. Poli, Eur. J. Inorg. Chem. (2004) 1081–1091;
(d) B.E. Ketz, A.P. Cole, R.M. Waymouth, Organometallics 23 (2004) 2835–2837;
(e) S.L. James, A.G. Orpen, P.G. Pringle, J. Organomet. Chem. 525 (1996) 299–301.