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Synthesis, characterisation and catalytic activity of Pd(II) and Ni(II) complexes with new cyclic α-diphenylphosphino-ketoimines. Crystal structure of 2,6-diisopropyl-*N*-(2-diphenylphosphino-cyclopentylidene)aniline and of 2,6-diisopropyl-*N*-(2-diphenylphosphino-cyclohexylidene)aniline

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Abstract

New cyclic α-diphenylphosphino-ketoimines have been synthesised by deprotonation of the corresponding imine and subsequent reaction with chlorodiphenylphosphine. The crystal structures of two of these compounds containing a cyclopentylidene and cyclohexylidene backbone are discussed. Reaction of these bidentate phosphorus–nitrogen (P^N) ligands with (cod)Pd(CH_3)Cl leads to neutral complexes of the general formula (P^N)Pd(CH_3)Cl which have been reacted with $AgSbF_6$ to yield cationic complexes of formula [(P^N)Pd(CH_3)($NCCH_3$)]SbF_6. Reaction of these ligands with (1,2-dimethoxyethane)$NiBr_2$ yields neutral nickel(II) complexes that have been characterised by IR and elemental analysis. Cationic Pd(II) complexes as well as MAO-activated neutral nickel(II) complexes have been used as ethylene oligomerisation catalysts. The cationic palladium(II) complexes show a marked pressure dependence of TOF, with α-olefin fraction and Schulz-Flory α-values explainable in the light of the accepted mechanism for analogous complexes. By increasing the steric bulkiness of the substituent on the imine, or by using ligands with cyclohexylidene or cycloheptylidene backbone instead of cyclopentylidene, a drop in catalytic activity is observed. Nickel(II) complexes of the title ligands activated with MAO permit to confirm the latter conclusions. In comparison with palladium their use brings to comparable linearities but higher oligomerisation grades as well as α-olefin fraction. Cationic palladium(II) complexes are also active in the propene and 1-butene oligomerisation.

Keywords: Palladium; Nickel; Methyl complexes; Phosphino ketoimines; Ethylene oligomerisation

1. Introduction

Bidentate ligands based on a phosphine and an additional donor atom such as oxygen, sulphur or nitrogen possess intriguing features [1]. Their importance mainly lies in the different *trans*-effect due to the different σ-donor and π-acceptor properties of phosphorus and of the heteroatom. This accounts for the importance of such ligands for applications in homogenous catalysis, for example the selectivity control in ethylene oligomerisation [2] or the CO migratory insertion into a Pd–CH_3 bond [3].

In this framework, P^N ligands are important because of their peculiar features [4]. Nitrogen donor atoms in most P^N bidentate ligands reported in the

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Nomenclature

cod	1,5-cyclooctadiene
dppCyPentMA	2,6-dimethyl-*N*-(2-diphenylphosphino-cyclopentylidene)aniline
dppCyPentPA	2,6-diisopropyl-*N*-(2-diphenylphosphino-cyclopentylidene)aniline
dppCyHexMA	2,6-dimethyl-*N*-(2-diphenylphosphino-cyclohexylidene)aniline
dppCyHexPA	2,6-diisopropyl-*N*-(2-diphenylphosphino-cyclohexylidene)aniline
dppCyHexMOA	2-methoxy-*N*-(2-diphenylphosphino-cyclohexylidene)aniline
dpptBuCyHexPA	2,6-diisopropyl-*N*-[4-*tert*-butyl-2-diphenylphosphino-cyclohexylidene)]aniline
dppCyHeptPA	2,6-diisopropyl-*N*-(2-diphenylphosphino-cycloheptylidene)aniline
dppHeptPA	2,6-diisopropyl-*N*-(2-diphenylphosphino-1-*n*-propyl-butylidene)aniline

literature bind to an aromatic system or are in the form of an amino- or imino- group. An important property of this class of compounds is the wide possibility to fine-tune the stereoelectronic features of the ligands, providing potential for tailoring. This advantage has been exploited for the synthesis of palladium and platinum complexes of several phosphino-imines [5]. The coordination of these P^N ligands is influenced by the phosphine functionality and by the σ-donor capacity of the lone pair on nitrogen while a π-coordination of the C=N double bond is only rarely observed in the case of imines [6]. Methyl palladium complexes of several phosphino-benzaldimines have been synthesised for a better understanding of an in situ ethylene oligomerisation catalytic system comprising palladium acetate, one equivalent of P^N ligand and two equivalents of *p*-tolyl-sulfonic acid [7]. Palladium complexes of *o*-(diphenylphosphino)-*N*-benzaldimine derivatives have recently received much attention as catalysts for the Heck reaction [8] as well as for the alkene/CO copolymerisation [9], also providing a useful insight into reaction mechanisms [10]. An interesting alternative to the P^N ligands with a benzaldimine backbone are ligands with pyrrolimine and dihydroxyoxazoline backbone which have originally been designed for asymmetric catalysis [11] and have recently been used in the palladium catalysed allylic substitution [12]. The inductive effect of these ligands has also been exploited for the CO/styrene [13] or CO/ethylene copolymerisation [14]. Phosphino-imines have also been used as ligands in the palladium catalysed alkynylstannylation [15] or in the alkoxycarbonylation [16] of alkynes. A phosphino-imine palladium complex was used as catalyst for the oxidative homocoupling reaction of organostannanes using air as oxidant [17]. Also cross-coupling of various types of aryl halides with alkynyl-, alkenyl- and arylstannanes have been catalysed by palladium(II) complexes with phosphino-imines [18]. Recently, the synthesis of an α-diphenylphosphino-ketoimine of formula $[Ph_2PCH_2C(Ph)=N(2,6\text{-}Me_2C_6H_3)]$ has been reported, together with the study of its palladium(II) complexes [19].

As part of our continuing interest in P^E ligands [20–23] (E = oxygen, sulphur or nitrogen), we lately started to investigate the behaviour towards palladium(II) and nickel(II) of α-diphenylphosphino ketoimines, the general formula of which is described in Fig. 1.

An α-diphenylphosphino-ketoimine derived from the linear ketone heptane-4-one has also been synthesised for comparison. The catalytic activity of their cationic palladium(II) complexes or of their nickel(II) complexes (the latter in association with MAO) in the ethylene oligomerisation reaction has also been investigated.

2. Results and discussion

2.1. Synthesis of phosphino ketoimines

The synthesis of the α-(diphenylphosphino)-ketoimines has been accomplished through condensation reaction between suitable ketones and anilines followed by α-deprotonation of the obtained ketoimines and reaction with P-chloro-diphenylphosphine. The synthesised ketoimines are reported in Table 1.

The deprotonation of an imine to yield an 1-aza-allyl anion is of great practical importance in organic chemistry [24]. Although the use of MeLi, *n*-BuLi or of Grignard reagents is generally not advisable because of the addition side-reactions that can occur to the C=N-Ar double bond, carrying out comparative syntheses using LDA and *n*-BuLi resulted in no difference in the final product. Since the use of LDA requires more difficult purification, *n*-BuLi was used as deprotonating agent. The steric hindrance of the formed imines is held responsible for the absence of addition reaction.

Contrary to the phosphino-imine reported by Green [19], where the formation of *E* and *Z* isomers in the

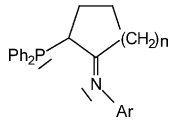
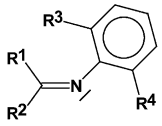


Fig. 1. α-(Diphenylphosphino) cyclic ketoimines (Ar = 2,6-dimethylphenyl or 2,6-diisopropylphenyl, *n* = 1–3).

Table 1
Ketoimines ***p-1*** –***p-8***



R^1, R^2	R^3	R^4	Label [b]
$-(CH_2)_4-$	Me	Me [a]	***p-1***
$-(CH_2)_4-$	*i*-Pr	*i*-Pr	***p-2***
$-(CH_2)_5-$	Me	Me [a]	***p-3***
$-(CH_2)_5-$	*i*-Pr	*i*-Pr	***p-4***
$-(CH_2)_5-$	H	OMe	***p-5***
$-(CH_2)_2-CH^tBu-(CH_2)_2-$	*i*-Pr	*i*-Pr	***p-6***
$-(CH_2)_6-$	*i*-Pr	*i*-Pr	***p-7***
n-C_3H_7, *n*-C_3H_7	*i*-Pr	*i*-Pr	***p-8***

[a] Literature known ketoimines (details are given in the Supplementary Material).
[b] See Section 3.

ratio 85:15 is reported, in our case the electrophilic attack of the chlorophosphine on the 1-aza-allyl anion takes place for steric reasons on the opposite side of the aryl functionality so that only the *anti*-substituted imine is formed as a racemate (Fig. 2). The imine form of the synthesised ligands is depicted in Table 2. Ligand **6**, which was synthesised in order to study the effect of reducing the ligand backbone flexibility on catalytic activity (vide infra), is obtained as a mixture of diastereoisomers.

Elemental analyses as well as mass spectrometry confirmed the proposed molecular formula for all ligands. Although in the solid state ligand **2** apparently exists only in the imine form (vide infra), solution NMR at room temperature supports an imine/enamine tautomery for the cyclopentylidene ligands **1** and **2**, as also recently observed for similar cyclic phosphino-ketoimines [25]. The equilibrium is shown in Fig. 3. The depicted enamine structure is in our opinion favoured by the possibility of further delocalisation on phosphorus. The $^{31}P\{^1H\}$ chemical shift of the phosphine functionality lies at $\delta = -6.6$ and -6.7 ppm, while for the enamine, values of $\delta = -30.3$ and $\delta = -30.5$ ppm are

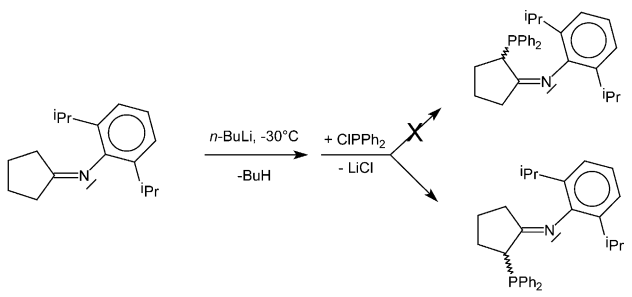


Fig. 2. Followed approach in the synthesis of α-(diphenylphosphino)-ketoimines exemplified for **2**.

observed for **1** and **2**, respectively. The ^{31}P-NMR integral ratio allows a rough evaluation of the imine/enamine ratio in $CDCl_3$ at 20 °C: 5.7 for **1** and 4.0 for **2**. Concerning the other synthesised ligands, the imine/enamine equilibrium was not observed in $CDCl_3$ solution for **3**, **4**, **7** and **8**, as monitored by $^{31}P\{^1H\}$-NMR spectroscopy.

2.2. Crystal structural aspects of ligands 2 and 4

The conformation of the new chelating ligands **2** and **4** has been disclosed by single crystal X-ray diffraction. The crystals have been obtained by precipitation from methanol and confirm the proposed imine structure. Ligands **2** and **4** crystallise in centrosymmetric space groups, i.e. as racemic crystals containing both *R* and *S* enantiomers. In Figs. 4 and 5 are shown the molecular structures of ligands **2** and **4**.

Geometrical parameters found in the structures of **2** and **4** and, in particular, the C=N bond distance [1.2588(17) Å in (**2**) and 1.267(2) Å in (**4**)], the $C(sp^3)$–P bond distance [1.8458(16) Å in (**2**) and 1.881(2) Å in (**4**)] are in the range found for analogous compounds [26]. A list of relevant crystallographic data is given in Table 3, while selected bond distances and angles are given in Table 4.

The cycloalkylidene backbone is in the thermodynamically favoured envelope conformation (**2**) or in the chair conformation (**4**). An almost perpendicular arrangement between the aromatic ring and the planes N1–C11–C12 (**2**) or N–C1–C2 (**4**) places the bulky isopropyl substituents above and below this latter plane. These conformations are compatible with the bis-imino ligands described by Brookhart and Gibson [27].

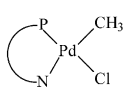
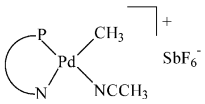
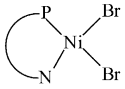
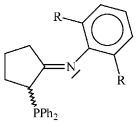
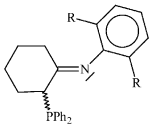
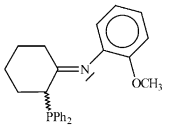
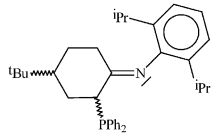
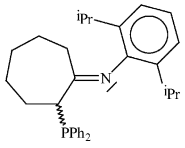
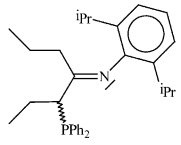
While κ^2-P,N coordination can occur for **2** without major ligand distortion, for compound **4** a ring inversion is required. Fig. 6 shows how the phosphine functionality is displaced from the axial to the equatorial position to permit a chelating coordination to the metal.

2.3. Neutral palladium(II) methyl complexes

The synthesised α-diphenylphosphino-ketoimines have been used as ligands for the preparation of the neutral palladium(II) complexes listed in Table 2. Methyl palladium complexes have been chosen because of their importance in catalytic C–C bond forming reactions. The synthetic approach envisages cyclooctadiene exchange by reaction of $(cod)Pd(CH_3)Cl$ with one equivalent of bidentate ligand, as depicted in Fig. 7. The main $^{31}P\{^1H\}$-, $^{13}C\{^1H\}$-NMR and IR spectroscopic features of all synthesised ligands and complexes are reported in Table 5.

All reported spectroscopic data for neutral complexes **9**, **12**, **15**, **18**, **21**, **23**, **26** and **29** prove a κ^2-P,N square planar coordination of the synthesised phosphino ke-

Table 2
Synthesised ligands and complexes

Ligands \ Complexes →		Neutral methyl Palladium(II) complexes 	Cationic methyl Palladium(II) complexes 	Neutral Nickel(II) complexes 
	R= CH_3 (**1**) dppCyPentMA	(**9**)	(**10**)	(**11**)
	R= ^{i}Pr (**2**) dppCyPentPA	(**12**)	(**13**)	(**14**)
	R= CH_3 (**3**) dppCyHexMA	(**15**)	(**16**)	(**17**)
	R= ^{i}Pr (**4**) dppCyHexPA	(**18**)	(**19**)	(**20**)
	(**5**) dppCyHexMOA	(**21**)	(**22**)	
	(**6**) lpptBuCyHexPA	(**23**)	(**24**)	(**25**)
	(**7**) dppCyHeptPA	(**26**)	(**27**)	(**28**)
	(**8**) dppHeptPA	(**29**)	(**30**)	(**31**)

toimines and a *cis* configuration of the methyl group with respect to phosphorus. A strong downfield shift in $^{31}P\{^1H\}$-NMR ranging from $\Delta\delta = 49.35$ ppm (**12**) to $\Delta\delta = 62.64$ ppm (**26**) with respect to the free ligand, clearly points out the coordination of phosphorus to palladium [28]. As expected on the basis of the comparison with similar phosphino-imine complexes [10b,10c], the coordination of the N donor atom can be clearly identified by a shift to lower wavenumbers in the IR spectra. The observed values are in the range $-46\ cm^{-1} < \Delta\nu(C{=}N) < -28\ cm^{-1}$. The imine coordination also causes a downfield shift of the $^{13}C{=}N$-signal.

Mass spectrometry analysis of the synthesised neutral complexes is straightforward by SIMS spectrometry in 3-nitrobenzylalcohol (NBA). In all cases, the highest molecular weight peak is seen as the anion $[M-1]^-$, thus ruling out the formation of chloro bridged dimeric complexes with κ^1-P coordination as was clearly shown by the same technique in the case of analogous palladium methyl complexes with the large byte bis–phosphine monoxide ligand dpppO. Other relevant peaks in the SIMS anion spectrogram of these complexes are the $[M-15]^-$ due to the loss of the methyl group, and different adducts of the chloride ion with the

Table 3
Crystal data, data collection parameters and convergence results for dppCyPentPA (**2**) and for dppCyHexPA (**4**)

	2	**4**
Empirical formula	$C_{29}H_{34}NP$	$C_{30}H_{36}NP$
Crystal size (mm)	$0.85 \times 0.53 \times 0.28$	$0.40 \times 0.48 \times 0.52$
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	16.8779(13)	10.610(2)
b (Å)	16.7624(13)	11.637(4)
c (Å)	18.4817(14)	12.044(4)
α (°)	90	72.33(3)
β (°)	97.356(3)	65.56(2)
γ (°)	90	86.80(2)
V (Å^3)	5185.7(7)	1285.7(7)
Z	8	2
Wavelength λ (Å)	0.71073	1.54184
Temperature (K)	293(2)	293
Scan type	ω	ω–2θ
Theta range for data collection (°)	1.54–27.45	4.0–70.0
Diffractometer	Bruker AXS SMART APEX	Nonius CAD4
Reflections collected	41 234	8366
Independent reflections	11 847 [$R_{int} = 0.0422$]	4862 [$R_{int} = 0.041$]
Reflection observed	6185 [$I > 2\sigma(I)$]	4212 [$I > 1\sigma(I)$]
Absorption correction	None	Numerical
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Hydrogen treatment	Riding with U_{iso} refined	Refined isotropically
Final R indices (observed data)	$R_1 = 0.0445$	$R = 0.064$
	$wR_2 = 0.1020$	$wR = 0.068$

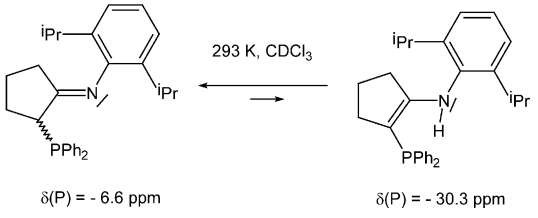


Fig. 3. Imine-enamine tautomeric equilibrium for ligand **2**.

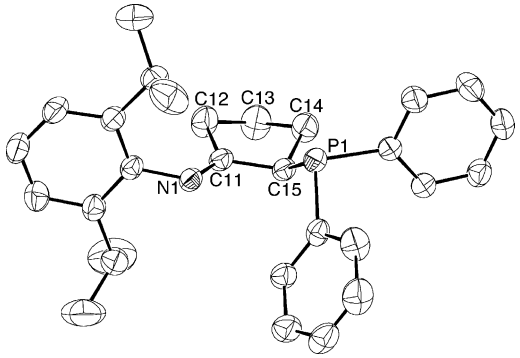


Fig. 4. Crystal structure of 2,6-diisopropyl-*N*-(2-diphenylphosphinocyclopentylidene)aniline (**2**).

Table 4
Selected bond distances (Å) and angles (°) for ligands (**2**) dppCyPentPA and (**4**) dppCyHexPA

	2		**4**
Bond distances [a]			
P1–C15	1.8458(16)	P–C6	1.881(2)
P1–C30	1.8366(16)	P–C21	1.832(2)
P1–C36	1.8253(18)	P–C31	1.843(2)
N1–C11	1.2588(17)	N–C1	1.267(2)
N1–C42	1.4242(17)	N–C11	1.429(2)
C11–C12	1.512(2)	C1–C2	1.515(2)
C12–C13	1.520(2)	C2–C3	1.534(3)
C13–C14	1.511(2)	C3–C4	1.527(3)
C14–C15	1.534(2)	C4–C5	1.519(3)
C15–C11	1.5109(19)	C5–C6	1.546(2)
		C6–C1	1.510(2)
Bond angle [a]			
C15–P1–C30	99.74(7)	C6–P–C21	103.11(8)
C15–P1–C36	103.49(8)	C6–P–C31	99.56(9)
C30–P1–C36	100.92(7)	C21–P–C31	102.70(8)
C11–N1–C42	119.69(12)	C1–N–C11	121.5(1)
N1–C11–C12	128.68(14)	N–C1–C2	126.7(2)
N1–C11–C15	121.93(13)	N–C1–C6	118.3(2)
C12–C11–C15	109.32(13)	C2–C1–C6	115.0(1)
C11–C12–C13	104.12(14)	C1–C2–C3	110.7(2)
C12–C13–C14	103.92(16)	C2–C3–C4	112.4(1)
C13–C14–C15	104.06(15)	C3–C4–C5	111.1(2)
C11–C15–C14	103.12(12)	C4–C5–C6	112.5(2)
P1–C15–C11	112.11(10)	C1–C6–C5	109.6 (2)
P1–C15–C14	114.58(12)	P–C6–C1	110.5(1)
P1–C36–C37	118.08(18)	P–C6–C5	109.8(1)

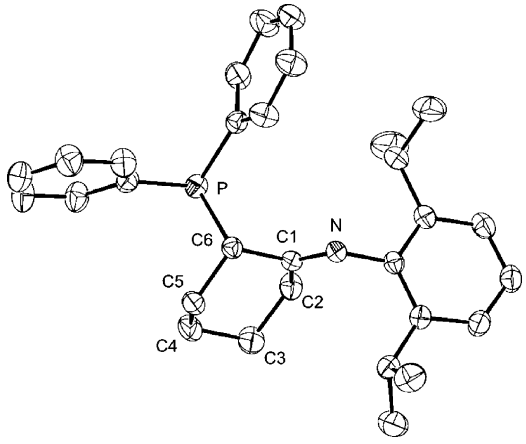


Fig. 5. Crystal structure of 2,6-diisopropyl-*N*-(2-diphenylphosphinocyclohexylidene)aniline (**4**).

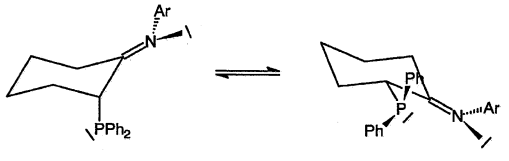
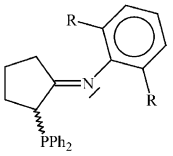
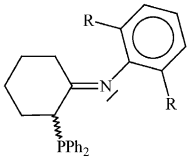
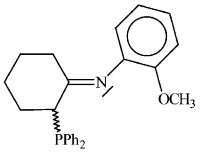
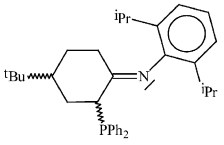
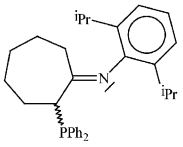
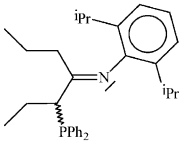


Fig. 6. Ring inversion of **4** favouring chelation on a metal centre (Ar = 2,6-diisopropyl-C_6H_3).

Table 5
Relevant spectroscopic data for ligands, and cationic palladium(II) complexes

		Ligand ^{31}P shift (ppm)	Ligand ν (C=N) (cm^{-1})	Ligand ^{13}C (C=N) (ppm)	Neutral complex ^{31}P shift (ppm)	Neutral complex ν (C=N) (cm^{-1})	Neutral complex ^{13}C (C=N) (ppm)	Cationic complex ^{31}P shift (ppm)	Cationic complex ν (C=N) (cm^{-1})	Cationic complex ^{13}C (C=N) (ppm)
	R: CH_3	-6.61 (**1**)	1676.6 (**1**)	180.5 (**1**)	43.17 (**9**)	1645.2 (**9**)	191.3 (**9**)	44.51 (**10**)	1661.0 (**10**)	195.8 (**10**)
	R: ^{i}Pr	-6.65 (**2**)	1677.1 (**2**)	180.2 (**2**)	42.70 (**12**)	1648.8 (**12**)	191.7 (**12**)	45.07 (**13**)	1653.4 (**13**)	195.7 (**13**)
	R: CH_3	-12.78 (**3**)	1653.0 (**3**)	173.8 (**3**)	49.60 (**15**)	1615.3 (**15**)	182.5 (**15**)	52.85 (**16**)	1622.7 (**16**)	186.0 (**16**)
	R: ^{i}Pr	-12.42 (**4**)	1650.8 (**4**)	173.1 (**4**)	49.78 (**18**)	1604.8 (**18**)	181.7 (**18**)	53.41 (**19**)	1620.8 (**19**)	185.5 (**19**)
		-10.17 (**5**)	1660.6 (**5**)	175.7 (**5**)	50.22 50.56 (**21**)	1618.0 (**21**)	183.0 183.8 (**21**)	53.07 (**22**)	1625.9 (**22**)	182.4 (**22**)
		-15.46 -8.35 (**6**)	1658.3 (**6**)	172.5 174.6 (**6**)	50.15 52.09 (**23**)	1616.1 (**23**)	181.9 184.3 (**23**)	53.66 54.00 (**24**)	1628.3 (**24**)	185.8 188.2 (**24**)
		-10.91 (**7**)	1637.2 (**7**)	175.9 (**7**)	51.73 (**26**)	1604.2 (**26**)	186.7 (**26**)	54.43 (**27**)	1606.9 (**27**)	188.8 (**27**)
		-2.95 (**8**)	1634.0 (**8**)	174.4 (**8**)	53.29 (**29**)	1599.5 (**29**)	184.2 (**29**)	55.72 (**30**)	1609.3 (**30**)	187.6 (**30**)

matrix. In the SIMS cation spectrogram, the highest molecular peaks observed are always due to the loss of chloride or of the methyl group.

A $^3J_{H,P}$ coupling constant ranging from 2.4 to 3.3 Hz for the doublet of the Pd–CH_3 protons in all methyl complexes except **26** can be invoked as a proof for the *cis* configuration of the methyl group relative to phosphorus, as the $^{13}C\{^1H\}$ chemical shift relative to the same fragment, which is shifted to $\delta \cong -4$ ppm [3a,5b] with respect to the precursor. Quite interestingly, **21** seems to be formed as a mixture of isomers in 1:1 ratio due to the unsymmetrical methoxy substituent on the phenyl ring, as evidenced by the appearance of two close Pd–CH_3 signals both in the ^1H ($\delta = 0.55$ and 0.56 ppm) and in the $^{13}C\{^1H\}$ spectrum ($\delta = -4.6$ ppm). Two singlets appear also for the OCH_3 signal both in the ^1H ($\delta = 3.70$ and 3.80 ppm) and in the $^{13}C\{^1H\}$ spectrum ($\delta = 55.9$ and 56.2 ppm). The corresponding signals in the $^{31}P\{^1H\}$ spectrum are at $\delta = 50.22$ and $\delta = 50.56$ ppm.

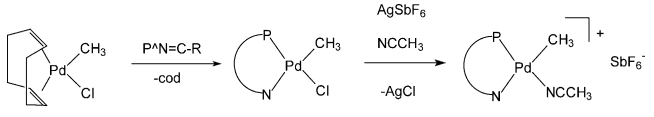


Fig. 7. Followed approach for the synthesis of neutral and cationic phosphino ketoimine complexes.

Table 6
Selected IR data for neutral complexes (P^N)$NiBr_2$

Number	(P^C=NR)$NiBr_2$ complex	(P^N)$NiBr_2$ ν(C=N)/cm^{-1}	$\Delta\nu$/cm^{-1} respect to ligand
11	(dppCyPentMA)$NiBr_2$	1642.6; 1625.9	−50.7; −34.0
14	(dppCyPentPA)$NiBr_2$	1642.8	−34.3
17	(dppCyHexMA)$NiBr_2$	1616.7	−36.3
20	(dppCyHexPA)$NiBr_2$	1616.2	−34.6
25	(dpptBuCyHexPA)$NiBr_2$	1619.9	−38.4
28	(dppCyHeptPA)$NiBr_2$	1595.4	−41.8
31	(dppHeptPA)$NiBr_2$	1571.1	−62.9

2.4. Cationic palladium(II) methyl complexes

Halogenide metathesis with $AgSbF_6$ in the presence of acetonitrile yielded the corresponding white or light-yellow cationic complexes listed in Table 2.

SIMS spectrograms obtained in DTT/DTE/Sul (see Section 3) point out that the palladium complexes are also monomeric species. Relevant signals are observed for all complexes at m/z values corresponding to $[(P\text{^}N)Pd(CH_3)]^+$ in the SIMS cation spectrogram (loss of the counteranion and of acetonitrile). The hexafluoroantimonate anion is seen as the only peak in the SIMS anion spectrogram ($m/z = 235$). Interestingly, for all complexes but **16** a complex matrix adduct of the kind $[(P\text{^}N)Pd + DTE/DTT - 1]^+$ is observed. All spectroscopic data reported for cationic complexes **10**, **13**, **16**, **19**, **22**, **24**, **27** and **30** confirm the κ^2-P,N square planar coordination and the *cis* configuration of the methyl group with respect to phosphorus. The $^3J_{H,P}$ coupling constant ranging from 1.2 to 2.1 Hz for the doublet of the Pd–CH_3 protons in almost all cationic methyl complexes synthesised clearly speaks for a retention of the *cis* configuration of the methyl group relatively to phosphorus after halide metathesis. The change in nature, from neutral to cationic complexes is held responsible for a stronger downfield shift in $^{31}P\{^1H\}$-NMR that ranges from $\Delta\delta = 51.1$ ppm to $\Delta\delta = 65.8$ ppm with respect to the free ligands. By comparing the $\Delta\nu$ values of C=N stretching frequencies for cationic complexes with respect to the free ligand, the $\Delta\nu$ values are in the range $-34.7\ cm^{-1} < \Delta\nu(C{=}N) < -15.6\ cm^{-1}$. This observation may tentatively be ascribed to a stronger back-donation to the coordinated imine in the case of neutral complexes. The observed shifts of the $^{13}C{=}N$-signals fall in the range 12.2 ppm < $\Delta\delta$ < 15.5 ppm with the exception of **22**, for which the $\Delta\delta(^{13}C{=}N)$ value is only 6.7 ppm. Stabilisation of all cationic methyl complexes by acetonitrile was monitored by IR. As expected for a large number of nitrile complexes in general [29], as well as for similar compounds [10b,10c], the two typical absorptions in the ν(C≡N)-region (2200–2260 cm^{-1}) caused by the CN stretching are shifted to higher wavenumbers (about 50 cm^{-1}) by *end-on* coordination to the metal. A strong band at about 658 cm^{-1} for the synthesised cationic complexes is clearly attributable to an octahedral hexafluoroantimonate anion. Of the P^N cationic complexes, only **24** is in the form of a diastereoisomeric mixture due to the presence of the ligand dpptBuCyHexPA (**6**). This aspect considerably complicates the ^1H- and $^{13}C\{^1H\}$-NMR interpretation of **24** and of its precursor **23**. However, based on $^{31}P\{^1H\}$-NMR, which clearly shows two signals at $\delta = 53.66$ and 54.00 ppm for **24**, and at $\delta = 50.15$ and 52.09 ppm for **23**, on IR data showing the expected red shift of the imine group [$-42.2\ cm^{-1}$ in the case of **23** and $-30.0\ cm^{-1}$ in the case of **24**], as well as on elemental and mass analysis, it is safe to assume for the above mentioned complexes, the structure proposed for the analogous neutral and cationic compounds.

2.5. Neutral nickel bromide complexes

Substitution of the weakly coordinating 1,2-dimethoxyethane in (dme)$NiBr_2$ with the P^N ligands permitted the obtainment of neutral nickel(II) complexes in quantitative yields. Selected IR data are summarised in Table 6. In analogy to the palladium(II) complexes described above, the chelation of the imine functionality is proven by a red-shift ($-63\ cm^{-1} < \Delta\nu < -34\ cm^{-1}$) of the C=N double bond stretching. Elemental analysis of the synthesised Ni(II) complexes is in accordance with the proposed structure.

2.6. Ethylene oligomerisation

In order to evaluate the potentiality of the new P^N ligands, their cationic palladium complexes have been used as catalyst for the ethylene oligomerisation reaction in homogeneous phase. The influence of ethylene pressure on activity and selectivity was first tested with complex **13** in the range 10 bar $\leq P \leq$ 60 bar. The results obtained by carrying out reactions at constant ethylene pressure are collected in Table 7.

From the reported data it is evident that, while the selectivity towards linear products does not considerably change in the explored range, by raising the pressure from 10 to 60 bars, a raise in catalyst activity (TOF

Table 7
Ethylene oligomerisation with **13**; influence of the pressure

Entry	P(ethylene) (bar)	TOF (h^{-1})	Linearity [a] (%)	Terminal olefin fraction [a] (%)	α [b]	C_{max}
1	10	312	89.5	25.7	0.54	14
2	20	407	88.8	26.8	0.66	16
3	30	662	88.1	29.0	0.61	20
4	40	822	89.1	31.1	0.69	22
5	50	1174	89.6	33.0	0.68	26
6	60	1337	90.5	34.8	0.72	26

Conditions: 0.05 mmol Pd; 20 ml CH_2Cl_2; $T = 70$ °C; $t = 2$ h.
[a] In the C_6-fraction.
[b] α = (mol C_{10}/mol C_8).

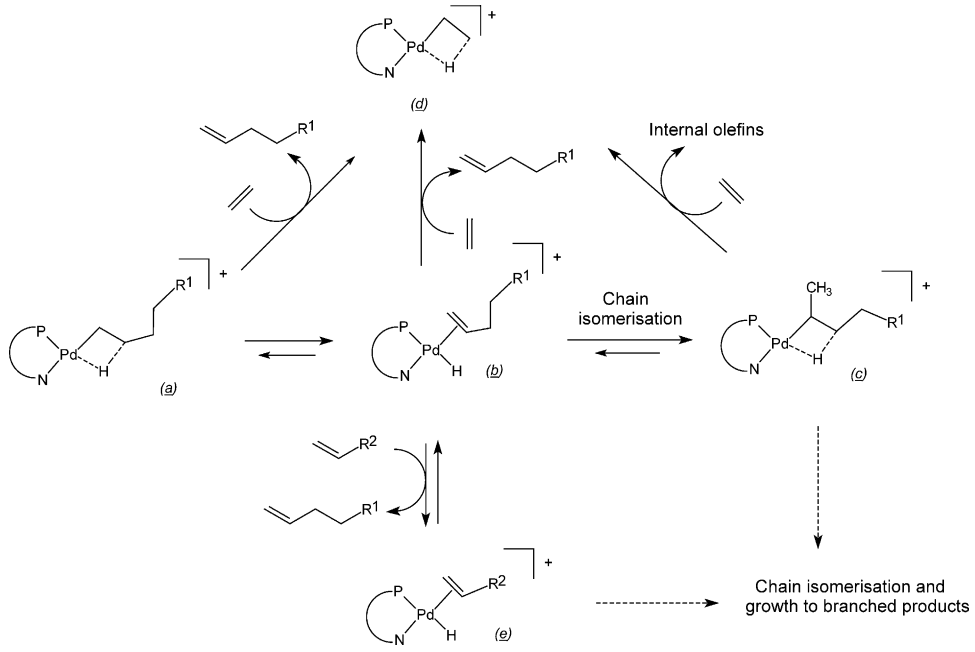


Fig. 8. Postulated reaction pathways explaining the pressure dependence of the α-olefin fraction in the Pd(II) catalysed ethylene oligomerisation with P^N ligands.

passing from 312 h^{-1} at 10 bars to 1337 h^{-1} at 60 bars), in selectivity towards α-olefin (passing from 25.7% at 10 bars to 34.8% at 60 bars), and in the Schulz–Flory α-value is observed. This behaviour is in agreement with the mechanism proposed by Brookhart for ethylene oligomerisation with diimine complexes [30], as explained below considering the possible mechanistic steps of isomerisation and chain transfer. Consequently to the raise in Schulz–Flory α-value, the C_{max} values are also positively influenced by pressure. These values are unusually high compared with similar cationic systems for ethylene oligomerisation [31] (Fig. 8).

Starting from the postulated metal-alkyl species exhibiting a β-agostic interaction (*a*) and (*c*) and from the hydride species (*b*), the chain transfer is controlled by ethylene concentration. The chain isomerisation starting from the hydride species (*b*), on the contrary is not dependent on the ethylene pressure. Correspondingly a higher ethylene pressure should in principle raise the ratio of the chain transfer rate versus isomerisation rate thus leading to higher α-olefin fractions. The ethylene pressure also influences the reinsertion of previously formed olefins [reaction (*b*) → (*e*)] that should also have less influence with raising the ethylene concentration. The possibility for reinsertion of previously formed olefins with consequent isomerisation was proven by the addition of an aliquot of 1-heptene to an ethylene oligomerisation run with **13** as a catalyst. As a result, 1-heptene was isomerised to internal heptenes without being converted to C_9- or higher alkenes. Furthermore, oligomerisation tests carried out with 1-hexene or 1-decene as substrates and **13** as catalyst, only resulted in very low oligomerisation grades and high isomerisation activity.

In order to check the results obtained and discussed for complex **13**, other catalysts have been used as

Table 8
Ethylene oligomerisation with cationic palladium(II) complexes; influence of the pressure

Entry	Complex	Ligand	P(ethylene) (bar)	TOF (h^{-1})	Linearity [a] (%)	Terminal olefin fraction [a] (%)	α [b]	C_{max}
1	**10**	dppCyPentMA	30	750	88.4	24.4	0.67	28
2	**10**	dppCyPentMA	40	1215	90.2	34.1	0.73	30
3	**19**	dppCyHexPA	30	155	84.4	25.3	– [c]	12
4	**19**	dppCyHexPA	40	424	84.4	29.7	0.65	16
5	**27**	dppCyHeptPA	30	331	70.6	31.4	0.67	14
6	**27**	dppCyHeptPA	40	398	75.2	35.6	0.72	16

Conditions: 0.05 mmol Pd; 20 ml CH_2Cl_2; $T = 70$ °C; $t = 2$ h.
[a] In the C_6-fraction.
[b] α = (mol C_{10}/mol C_8).
[c] Not determined because of the low conversion.

comparison at 30 and 40 bar of ethylene pressure. The results are collected in Table 8.

On raising the ethylene pressure, complexes **10**, **19** and **27**, which differ from **13** in steric hindrance on nitrogen [2,6-dimethylphenyl (**10**)] or in the cycloalkylidene size [cyclohexylidene (**19**), cycloheptylidene (**27**)], show the expected raise in TOF, α-fraction and C_{max} (comparison of entries 1 and 2, 3 and 4, 5 and 6). TOF rises dramatically with pressure for complexes **10** and **19** while for complex **27** a limited effect is observed probably because of the more flexible backbone. The pressure effect on α-fraction is more evident for complex **10** (from 24.4 to 34.1% entries 1 and 2 of Table 8). The percentage of linear products remains almost unchanged for complexes **10** and **19**, only for complex **27** a raise from 70.6 to 75.2% being observed.

The steric crowding in the vicinity of the catalytic active site may have a considerable effect on activity and selectivity [32]. All literature results point out a blocking of the axial position on the metal through the bulky ligands therefore avoiding the approach of ethylene from one of these positions, consequently bringing to higher rates for β-H-elimination. These effects should in principle be noticeable also by using α-diphenylphosphino-ketoimines catalyst precursors. Moreover, as is known for P^O-nickel complexes [33], the limitation of ligand backbone flexibility brings to higher catalyst selectivities and oligomerisation grades. In order to obtain other clues for this behaviour of palladium complexes with α-diphenylphosphino-ketoimine, ligands forming five terms metallacycle but with different ligand backbone have been used in catalysis. In this study, summarised in Table 9, cyclic as well as open-chain hydrocarbons have been used as backbone. For the sake of comparison, entries 1, 2 and 4, that have already been discussed, are reported again in Table 9.

Noteworthy, changing the *ortho*-substituents on the aniline from methyl to *iso*-propyl (comparison of entries 1 and 2 and of entries 3 and 4) points out an almost identical selectivity to linear products and a slightly higher activity and oligomerisation grades for the less crowded complexes **10** and **16**. Interesting results have been obtained with **22** bearing a methoxy functionality. Not only are the TOFs above the average, and $C_{max} >$ 30 carbon atoms, but also very high selectivity to linear products (> 96%) distinguishes the catalyst. The methoxy group is to be held responsible for these characteristics. The reasons may be: (a) a different basicity of the nitrogen donor atom, due to mesomeric effects, although this should not, in comparison with the alkyl substituted derivatives, cause any major difference; (b) an interaction of the methoxy oxygen atom with the metal centre. This latter effect could directly influence the electronic properties on palladium but it could also bring to the blocking of one of the axial positions by interaction of the methoxy group lone pair with the metal centre during the catalytic cycle.

As to ligand backbone variation, comparing entry 1 with 3 and entries 2 with 4 (same steric hindrance on nitrogen) the effect of enlarging ligand backbone from cyclopentylidene to cyclohexylidene clearly shows the two aforementioned effects: while linearities are slightly but significantly affected (from 88 to 84% on average thus evidencing a reduced chelate control consequent to higher ligand backbone flexibility), the effect on α-fraction seems to be clear only for complexes **10** and **16** (entries 1 and 3 of Table 9: 24.4 and 32.8%, respectively). By reducing backbone flexibility of the cyclohexylidene structure by embodying a *t*-butyl group into it as in **24** (entry 6, Table 9), a slightly higher TOF and C_{max} were obtained, while product linearity and α-fraction are unchanged with respect to **19** (entry 4, Table 9). The results obtained with complex **27** bearing a cycloheptylidene backbone (entry 5, Table 8) showed a markedly lower product linearity although both activity and oligomerisation grades were slightly higher than for **19**. Using an open chain alkylidene backbone, as in complex **30**, has the expected effect of a marked lowering in activity, to the point that a chromatographic analysis to assess selectivity was hampered (entry 7, Table 9).

Table 9
Ethylene oligomerisation with cationic palladium(II) complexes. Influence of ligand backbone and steric hindrance

Entry	Complex	Ligand	TOF (h^{-1})	Linearity [a] (%)	Terminal olefin fraction [a] (%)	α [b]	C_{max}
1	**10**	dppCyPentMA	750	88.4	24.4	0.67	28
2	**13**	dppCyPentPA	662	88.1	29.0	0.61	20
3	**16**	dppCyHexMA	314	83.8	32.8	0.71	18
4	**19**	dppCyHexPA	155	84.4	25.3	– [c]	12
5	**22**	dppCyHexMOA	1034	96.6	52.3	0.74	34
6	**24**	dpptBuCyHexPA	258	83.1	27.5	0.48	16
7	**30**	dppHeptPA	225	– [c]	– [c]	0.51	12

Conditions: 0.05 mmol Pd; 20 ml CH_2Cl_2; 30 bar ethylene, $T = 70$ °C; $t = 2$ h.
[a] In the C_6-fraction.
[b] α = (mol C_{10}/mol C_8).
[c] Not determined because of the low conversion.

Table 10
Ethylene oligomerisation with the in situ catalytic system (P^N)$NiBr_2$/MAO

Entry	Complex		TOF (h^{-1})	Linearity	Terminal olefin fraction [a] (%)	α [b]	C_{max}
1	**11**	(dppCyPentMA)$NiBr_2$	29 500	84.3	49.1	0.83	30
2	**14**	(dppCyPentPA)$NiBr_2$	8420	85.0	33.1	0.83	28
3	**17**	(dppCyHexMA)$NiBr_2$	10 900	86.1	36.4	n.det.	28
4	**20**	(dppCyHexPA)$NiBr_2$	2750	82.9	43.6	0.85	30
5	**25**	(dpptBuCyHexPA)$NiBr_2$	3100	84.8	50.0	0.95	30
6	**28**	(dppCyHeptPA)$NiBr_2$	4600	80.6	45.2	0.93	28
7	**31**	(dppHeptPA)$NiBr_2$	5540		Waxes		

Conditions: 0.02 mmol Ni; 100 eq. MAO; 20 ml toluene; 30 bar ethylene; $T = 50$ °C; $t = 2$ h.

The results described here point to a chelate control of the reaction which brings to a loss in catalyst activity and selectivity on raising the flexibility of the ligand backbone: a continuous decrease in selectivity towards linear products is observed passing from cyclopentylidene (entry 2 Table 9: 88%) to cyclohexylidene (entry 4 Table 9: 84%) or to cycloheptylidene (entry 5 Table 8: 71%). The catalytic results seem to point out to the formation, in the case of more flexible rings, of more stable and catalytically inactive complexes. Blocking the catalyst flexibility of the cyclohexylidene backbone by a *t*-butyl group has only a minor beneficial effect on catalyst activity but does not modify dramatically the catalyst selectivity (comparison of entries 4 and 6, Table 9).

2.7. Ethylene oligomerisation with nickel dibromide complexes activated with MAO

In order to check the potentiality of the α-diphenylphosphino-ketoimine ligands also in the nickel(II) catalysed homogeneous ethylene oligomerisation, the P^N nickel dibromide complexes have been used as catalysts with MAO as activating agent. Results are collected in Table 10. All systems tested show much higher activity compared to their analogous palladium catalysts.

A first remark concerns the catalyst activity and confirms an observation previously pointed out for palladium catalysts: comparing activities in entries 1 and 2, as well as in 3 and 4 (Table 10), a drop in TOF is observed for complexes with phosphino ketoimines bearing the sterically crowded diisopropyl group.

In analogy with results obtained with cationic palladium complexes, comparison of entry 1 with entry 3 and of entry 2 with entry 4 shows a drop in catalytic activity consequent to backbone enlargement from cyclopentylidene to cyclohexylidene. The highest activity is reached for complex **11** (entry 1, Table 10) which also permits the obtainment of highly linear (84.3%) terminal olefins (49%) with high oligomerisation grade ($C_{max} = 30$).

Using cycloheptylidene [**28**, entry 6] or "blocked" cyclohexylidene backbone [**25**, entry 5] has no dramatic influence neither on TOF nor on selectivities or on C_{max}. Unexpectedly, the use of complex **31** bearing the open chain heptylidene brings to the formation of waxes (Table 10, entry 7), in contrast with its palladium analogue which is sparingly active as oligomerisation catalyst (Table 9, entry 7).

2.8. Oligomerisation of higher olefins

The activity of the cationic palladium complexes was also tested in the oligomerisation of higher olefins by

Table 11
Oligomerisation of propene with cationic palladium(II) complexes

Entry	Complex	Ligand	TOF (h^{-1})	Linearity [a] (%)	C_{max}
1	**10**	dppCyPentMA	75.1	43.4	18
2	**13**	dppCyPentPA	37.8	55.5	15
3	**16**	dppCyHexMA	22.8	33.6	15
4	**19**	dppCyHexPA	3.4	44.1	12
5	**22**	dppCyHexMOA	22.3	42.5	9
6	**24**	dpptBuCyHexPA	11.1	45.7	12
7	**27**	dppCyHeptPA	5.4	36.8	12
8	**30**	dppHeptPA	1.4	– [b]	9

Conditions: 0.05 mmol Pd; 20 ml CH_2Cl_2; 0.2 mol propene; $T = 70$ °C; $t = 16$ h.
[a] In the C_6-fraction.
[b] Not determined because of the low conversion.

Table 12
1-Butene-oligomerisation with cationic palladium(II) complexes

Entry	Complex	Ligand	TOF (h^{-1})	Linearity [a]			C_{max}
				C_8%	C_{12}%	C_{16}%	
1	**10**	dppCyPentMA	2.5	34.8	5.2	3.1	16
2	**13**	dppCyPentPA	12.9	53.8	28.8	14.2	16
3	**16**	dppCyHexMA	1.1	– [b]	– [b]	–	12

0.05 mmol Pd; 20 ml CH_2Cl_2; 0.1 mol 1-butene; $T = 70$ °C; $t = 16$ h.
[a] In the C_x-fraction (determined after hydrogenation).
[b] Not determined because of the low conversion.

conducting batch tests under the conditions optimised for the ethylene oligomerisation. The reaction time was prolonged to 16 h because of the lower activity of the substrates. The oligomerisation of propene was carried out in dichloromethane at 70 °C. The results are collected in Table 11.

Complexes **10** and **13** that embody a cyclopentylidene backbone, are more active then their homologues based on a cyclohexylidene **16** and **19** or cycloheptylidene **27** structure. Complex **22** bearing the *o*-methoxy substituted ligand shows a scarce oligomerisation grade combined with a moderate activity. A drop in catalytic activity is shown by complexes **13** and **19** compared to complexes **10** and **16**, as a result of a higher steric hindrance on palladium. The importance of a certain backbone rigidity in the chelate control is evidenced by entry 8: complex **30** is practically inactive in the propene oligomerisation. It is interesting to note again how reducing the ligand backbone flexibility by the *t*-butyl group in complex **24** has the effect of raising the catalyst activity (comparison of entry 6 with entry 4).

The most active complexes in the propene oligomerisation, **10**, **13** and **16**, have been tested in the 1-butene oligomerisation. Results have been collected in Table 12. It is evident, by comparing TOFs of Table 12 with those of Table 11, that the catalytic activity is lowered. The sterically hindered dppCyPentPA complex **13** shows in this case the highest TOF (entry 2). Products up to 16 C-atoms are obtained. The reaction solution does not show signs of decomposition through Pd(0) formation. Reducing the crowding on the imine substituent (entry 1) or using the more flexible cyclohexylidene backbone (entry 3) dos not bring a beneficial effect on the catalytic activity.

Surprisingly, the fraction of linear products is relatively high, in particular in the trimer and tetramer fraction. The formation of linear dimers can be deduced directly from the insertion mechanism, but for the formation of linear trimers a palladium-alkyl isomerisation must first occur. Fig. 9 represents a possible reaction pathway for the formation of butene linear trimers.

A palladium-*iso*-alkyl compound can be formed by a 1,2- and subsequent 2,1- insertion of 1-butene in a palladium hydride species. The palladium atom is localised on the third carbon atom. If a β-elimination takes place now, then 2-octene or 3-octene can be formed. On the contrary, if a chain growth takes place through another butene insertion, the formation of branched trimers is inevitable. The formation of linear trimers of 1-butene can only be explained in terms of isomerisation of the palladium-*iso*-alkyl species by *chain walking* to a stable *n*-octyl palladium intermediate before the necessary 2,1-insertion of the third butene takes place [34].

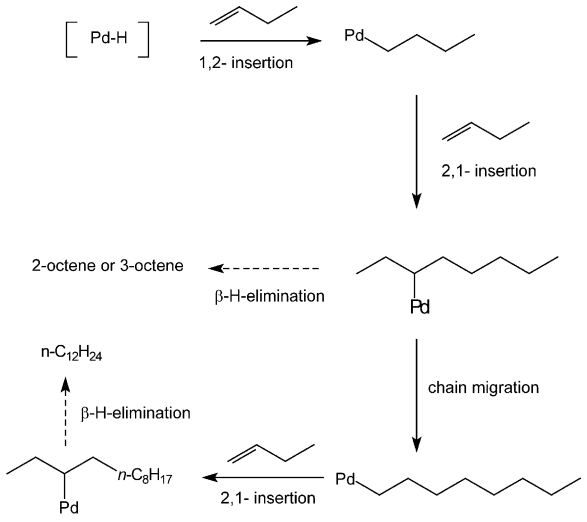


Fig. 9. Mechanism of formation of linear trimers of 1-butene with cationic Pd (II) complexes. The ligand and the charge of the intermediate species have been omitted for clarity.

3. Experimental

3.1. General procedures and techniques

All procedures were routinely performed under pure dry Ar using standard Schlenk techniques. ^{1}H-, ^{13}C{^{1}H}-, and ^{31}P{^{1}H}-NMR spectra were recorded on a Bruker DPX 300 NMR spectrometer at 293 K. ^{31}P-NMR chemical shifts relative to 85% phosphoric acid are reported with positive values downfield from the reference. IR spectra were recorded on a Nicolet 510 P FT spectrometer. For secondary ion mass spectra (SIMS), obtained on a Finnigan MAT 95 spectrometer, the samples were prepared as dispersion in 3-nitrobenzylalcohol (NBA), or in a mixture of 1,4-dithio-DL-threitol, 1,4-dithioerythritol, sulfolane (DTT/DTE/Sul). Mass spectra of vaporisable solids (P^N-ligands) have been recorded on a Varian MAT 112 S (E.I. = 70 eV, 210 °C, 2×10^{-6} Torr). The attributions of the fragmentation pattern have been assigned through comparison of isotopic abundance of ions with those calculated from isotopic abundance of elements. Elemental analyses were performed on a Carlo Erba 1106 CHN-Analyser. Single crystal X-ray diffraction studies were carried out on Nonius CAD4 instruments equipped with serial scintillation counters and a Bruker-AXS SMART diffractometer with an APEX CCD detector.

If not otherwise specified, all solvents were purified by common laboratory techniques and distilled prior to use under a stream of Ar; deionised water was repeatedly degassed with a water pump under ultrasound stirring and eventually saturated with Ar. Deuterated solvents for NMR spectroscopy have been purchased from Aldrich and kept under Ar [35]. 2,6-Dimethyl-aniline, 2,6-diisopropyl-aniline, *o*-anisidine, $AgSbF_6$ (97%), (dme)$NiBr_2$ (97%) were purchased from Aldrich; tetramethyltin was purchased from Fluka; P-chlorodiphenylphosphine (95%) was purchased from Strem. Reagents were used as received.

Palladium complexes (cod)$PdCl_2$ [36], [(cod)-Pd(CH_3)Cl] [37] have been synthesised following literature procedures. Palladium chloride was furnished by Degussa AG. MAO was purchased from WITCO as 10% toluene solution (6–8% MAO and 2–4% trimethylaluminum), ethylene 2.8 (99.8% purity) was purchased from Gerling, Holz & Co. Reagents were used as received.

Gas-chromatograms were obtained on Siemens Synchromat systems equipped with a 25 m SE 54-CS column using nitrogen as carrier gas, or with a 100 m Pona CB using helium as carrier gas. Yields of ethylene oligomers were obtained with the use of the internal standard method (nonane). In the GC analytic an FID detector was used. Concerning the determination of linearity and quantity of 1-hexene in the C_6-fraction, after having removed high boiling products by *flash* distillation at room temperature the separation of the C_6-fraction was performed on a Siemens Sichromat 1-4 instrument equipped with a 50 m Pona-HP-FS column. Turn over frequencies (TOF) was calculated as [mole consumed monomer/(mole catalyst · time)].

3.2. General procedure for the synthesis of ligands *1*–*8*

3.2.1. General procedure A

The alkylidene anilines were obtained by condensation from a ketone and an aniline. The reaction was driven to completion by azeotropic distillation of water.

A 250 ml round flask was added of 0.1 mol of substituted aniline, 0.11 mol of ketone, 0.3 g (1.7 mmol) of *p*-tolyl sulphonic acid and 200 ml of toluene as stripping agent. The mixture was kept under vigorous stirring and refluxed with a water extractor for at least 6 h, in most cases overnight, until no more water was formed. Eventually, the major part of the solvent was distilled at normal pressure and the residue on a Vigreux column under reduced pressure. The alkylidene anilines (mostly obtained as very viscous liquids) have been stored under argon at −30 °C.

Spectroscopic data for the obtained ketoimines have been deposited as supplementary material.

3.3. Synthesis of α-(diphenylphosphino)-ketoimines

3.3.1. General procedure B

In a round flask, 10 mmol of substituted alkylidene aniline are solubilised in 20 ml *n*-pentane and 5 ml Et_2O or THF, cooled at −30 °C and kept under vigorous stirring. An equivalent quantity of a solution of *n*-BuLi in hexanes was added dropwise and the reaction mixture warmed to 0 °C in about 2 h. Incipient precipitation is

dissolved with the addition of a few millilitres of THF. The now yellow mixture is again cooled at −30 °C and at this temperature 1.0 equivalent of P-chlorodiphenylphosphine is added dropwise over a 30' time, so that the incipient red colour has disappeared before the next drop is added. When all reagents are mixed, the reaction vessel is warmed to room temperature (r.t.) and kept under overnight stirring. The yellow suspension is diluted with 20 ml of Et_2O and washed with 2×20 ml water. The organic phase is separated and dried over sodium sulphate. The solvent is eventually evaporated in vacuo. In some of the syntheses the P^N ligand precipitates as a yellow solid that is purified by washing with *n*-pentane. In general, the obtained yellow–orange oils are diluted with methanol, *n*-pentane or THF and kept at −10 °C for crystallisation.

3.3.2. 2,6-Dimethyl-N-(2-diphenylphosphino-cyclopentylidene)aniline; dppCyPentMA (**1**)

The synthesis of the ligand was performed following general procedure B described above starting from 5.62 g (30.01 mmol) of substituted alkylidene aniline ***p-1***, 19 ml of a 1.6 M *n*-BuLi-solution and 6.28 g (28.46 mmol) $ClPPh_2$. Yield: 5.07 g (13.64 mmol, 48%) of an off-white solid, obtained by crystallisation from MeOH. Anal. Found: C, 80.91; H, 7.10; N, 3.82. Calc. for $C_{25}H_{26}NP$: C, 80.84; H, 7.06; N, 3.77%. The compound is subject to a r.t. imine to enamine tautomer equilibrium ratio of about 6:1. ^{1}H-NMR ($CDCl_3$, 300 MHz): [ppm] $\delta =$ 1.55–2.25 (br m, 6H, CH_2), 1.81 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 3.56 (dt, $J_{H,H} = 4.2$ Hz, $J_{H,P} = 7.8$ Hz, 1H, PCH), 6.74–7.65 (m, 13H, H_{arom}); $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75 MHz) [ppm]: $\delta = 17.9$, 18.0 (CH_3), 23.2 (d, $J_{C,P} = 6.6$ Hz, CH_2), 29.0 (d, $J_{C,P} = 9.4$ Hz, CH_2), 31.7 (CH_2), 45.0 (d, $J_{C,P} = 16.3$ Hz, PCH), 122.4, 127.7–134.7 (CH_{arom}), 125.9, 125.7, 137.1–138.5 (C_{ipso}), 150.0 (NC_{ipso}), 180.5 (d, $J_{C,P} = 10.5$ Hz, C=N); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121 MHz): [ppm] $\delta = -6.61$ (s, ca. 0.85P, $Ph_2P\hat{}C{=}NAr$), −30.27 (s, ca. 0.15P, $Ph_2P\hat{}C{-}NHAr$); IR (KBr): [cm^{-1}] $\nu = 1676.6$ (s, C=N); MS: *m/z* ($I_{rel.}$/%) = 372 (10) $[M+1]^+$, 371 (33) $[M]^+$, 357 (20) $[M+1-CH_3]^+$, 356 (100) $[M-CH_3]^+$, 199 (15), 186 (54) [M − PPh_2 or PPh_2+1]$^+$, 185 (66) $[PPh_2]^+$,184 (33), 183 (35), 144 (18), 109 (18), 108 (32), 105 (26) $[C_8H_9]^+$, 91 (15) $[C_7H_7]^+$, 79 (34), 77 (33) $[C_6H_5]^+$.

3.3.3. 2,6-Diisopropyl-N-(2-diphenylphosphino-cyclopentylidene)aniline; dppCyPentPA (**2**)

The synthesis of the ligand was performed following general procedure B starting from 10.22 g (41.99 mmol) substituted alkylidene aniline ***p-2***, 26.0 ml of a 1.6 M *n*-BuLi solution and 9.00 g (40.79 mmol) $ClPPh_2$. Suitable crystals for X-ray diffraction analysis have been obtained by precipitation from MeOH. Yield: 8.37 g (19.58 mmol, 48%) of colourless crystals obtained by crystallisation from methanol. Anal. Found: C, 81.54; H, 8.10; N, 3.35. Calc. for $C_{29}H_{34}NP$: C, 81.46; H, 8.02; N, 3.28%. The compound is subject to a r.t. imine to enamine tautomer equilibrium ratio of about 4:1. ^{1}H-NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 0.84$, 1.05, 1.06, 1.10 (4*d, $J = 6.9$ Hz, 4*3H, CH_3^{iPr}), 1.51–2.26 (m, 6H, CH_2), 2.65, 2.72, 3.29 (hept., $J = 6.9$ Hz, 2H, CH^{iPr}), 3.59 (m, 0.8H, PCH), 6.05 (d, $J = 5.7$ Hz, 0.2H), 6.88–7.68 (m, 13H, H_{arom}); $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75 MHz, only data for the main isomer are given) [ppm]: $\delta = 22.7$, 22.9 (CH_3), 23.4 (d, $J_{C,P} = 6.4$ Hz, CH_2), 23.5, 23.6 (CH_3), 27.8, 28.2 (CH^{iPr}), 28.9 (d, $J_{C,P} = 10.1$ Hz, CH_2), 31.9 (CH_2), 44.6 (d, $J_{C,P} = 16.6$ Hz, PCH), 122.7–134.6 (CH_{arom}), 135.3–138.6 (C_{ipso}), 147.6, 147.8 (NC_{ipso}), 180.2 (d, $J_{C,P} = 10.5$ Hz, C=N); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121 MHz): [ppm] $\delta = -6.65$ (s, ca. 0.8P, $Ph_2P\hat{}C{=}NAr$), −30.45 (s, ca. 0.2P, $Ph_2P\hat{}C{-}NHAr$); IR (KBr): [cm^{-1}] $\nu = 1677.1$ (s, C=N); MS: *m/z* ($I_{rel.}$/%) = 427 (5) $[M]^+$, 412 (16) $[M-CH_3]^+$, 385 (30) $[M+1-C_3H_7]^+$, 384 (100) $[M-C_3H_7]^+$, 242 (5) [M − PPh_2]$^+$, 226 (8) $[CH_2CH_2CHPPh_2]^+$, 201 (8) $[CH_2CNAr]^+$, 183 (10) $[CNAr]^+$, 108 (6), 91 (7) $[C_7H_7]^+$, 77 (5) $[C_6H_5]^+$, 43 (9) $[C_3H_7]^+$.

3.3.4. 2,6-Dimethyl-N-(2-diphenylphosphino-cyclohexylidene)aniline; dppCyHexMA (**3**)

The synthesis of the ligand was performed following general procedure B starting from 3.28 g (16.29 mmol) substituted alkylidene aniline ***p-3***, 10 ml of a 1.6 M *n*-BuLi solution and 3.60 g (16.32 mmol) $ClPPh_2$. The product precipitates as white solid, is filtered, washed with *n*-pentane and crystallised from THF–Et_2O. Yield: 3.86 g (10.01 mmol, 61%). Anal. Found: C, 80.95; H, 7.28; N, 3.61. Calc. for $C_{26}H_{28}NP$: C, 81.01; H, 7.32; N, 3.63%. ^{1}H-NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 1.45$–2.10 (m, 7H, CH_2), 1.47 (s, 3H, CH_3), 1.78 (s, 3H, CH_3), 2.24–2.37 (m, 1H, CH_2), 3.62 (dt, $J_{H,H} = 5.4$ Hz, $J_{H,P} =$ 11.4 Hz, 1H, PCH), 6.69–7.68 (m, 13H, H_{arom}). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75 MHz): [ppm] $\delta = 17.7$, 18.1 (CH_3), 23.8 (d, $J_{C,P} = 8.7$ Hz, CH_2), 27.8 (CH_2), 30.7 (d, $J_{C,P} = 3.5$ Hz, CH_2), 31.1 (d, $J_{C,P} = 11.1$ Hz, CH_2), 47.3 (d, $J_{C,P} = 11.9$ Hz, PCH), 122.3, 127.5, 127.6, 128.2–134.2 (CH_{arom}), 126.1 (MeC_{ipso}), 137.0 (d, $J_{C,P} = 11.8$ Hz, PC_{ipso}), 137.8 (d, $J_{C,P} = 16.0$ Hz, PC_{ipso}), 148.2 (NC_{ipso}), 173.8 (d, $J_{C,P} = 9.9$ Hz, C=N); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121 MHz): [ppm] $\delta = -12.78$ (s); IR (KBr): [cm^{-1}] $\nu = 1653.0$ (s, C=N); MS: *m/z* ($I_{rel.}$/%) = 386 (15) $[M+1]^+$, 385 (47) $[M]^+$, 371 (24) $[M+1-CH_3]^+$, 370 (100) $[M-CH_3]^+$, 277 (18), 276 (46), 200 (29) [M − PPh_2]$^+$, 199 (37), 185 (22) [PPh_2, M − PPh_2_CH_3]$^+$, 183 (30), 172 (15) [M − PPh_2_C_2H_4]$^+$, 158 (23) [M − PPh_2_C_3H_6]$^+$, 145 (21), 108 (15), 105 (25) $[C_8H_9]^+$, 79 (23), 77 (27) $[C_6H_5]^+$, 41 (26) $[C_3H_5]^+$, 27 (16) $[C_2H_3]^+$.

3.3.5. 2,6-Diisopropyl-N-(2-diphenylphosphino-cyclohexylidene)aniline; dppCyHexPA (4)

The synthesis of the ligand was performed following general procedure B starting from 5.74 g (22.28 mmol) substituted alkylidene aniline ***p-4***, 14.5 ml of a 1.6 M *n*-BuLi-solution and 4.90 g (22.21 mmol) $ClPPh_2$. The addition of *n*-pentane to the yellow crude caused the product precipitation. Suitable crystals for X-ray diffraction analysis have been obtained by precipitation from methanol at −20 °C. Yield: 6.18 g (13.99 mmol, 63%) of colourless powder or crystals. Anal. Found: C, 81.68; H, 8.27; N, 3.20. Calc. for $C_{30}H_{36}NP$: C, 81.60; H, 8.22; N, 3.17%. ^{1}H-NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 0.79, 0.84, 0.87, 1.00$ (4*d, $J = 6.9$ Hz, 4*3H, CH_3^{iPr}), 1.42–2.02 (m, 7H, CH_2), 2.27 (hept., $J = 6.9$ Hz, 1H, CH^{iPr}), 2.29–2.41 (m, 1H, CH_2), 2.47 (hept., $J = 6.9$ Hz, 1H, CH^{iPr}), 3.59 (dt, $J_{H,H} = 6.3$ Hz, $J_{H,P} = 11.4$ Hz, 1H, PCH), 6.84–7.68 (m, 13H, H_{arom}); $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75 MHz): [ppm] $\delta = 23.1$, 23.3, 23.5, 23.6 (CH_3), 23.9 (d, $J_{C,P} = 8.7$ Hz, CH_2), 27.2 (CH_2), 27.4, 27.5 (CH^{iPr}), 30.7 (d, $J_{C,P} = 10.7$ Hz, CH_2), 31.1 (d, $J_{C,P} = 2.8$ Hz, CH_2), 47.0 (d, $J_{C,P} = 12.1$ Hz, PCH), 122.5–134.3 (CH_{arom}), 136.6, 136.7 ($^iPrC_{ipso}$), 137.2 (d, $J_{C,P} = 11.8$ Hz, PC_{ipso}), 138.0 (d, $J_{C,P} = 16.5$ Hz, PC_{ipso}), 145.4 (NC_{ipso}), 173.1 (d, $J_{C,P} = 10.3$ Hz, C=N); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121 MHz): [ppm] $\delta = -12.42$ (s); IR (KBr): [cm^{-1}] $\nu = 1650.8$ (s, C=N); MS: *m/z* ($I_{rel.}$/%) = 441 (5) $[M]^+$, 426 (7) $[M-CH_3]^+$, 399 (29) $[M+1-C_3H_7]^+$, 398 (100) $[M-C_3H_7]^+$, 256 (9) $[M-PPh_2]^+$, 240 (19) $[(CH_2)_3CHPPh_2]^+$, 212 (11) $[CH_2CHPPh_2]^+$, 186 (10) $[398-212]^+$, 185 (9) $[PPh_2]^+$, 183 (14), 108 (9), 91 (9) $[C_7H_7]^+$, 77 (7) $[C_6H_5]^+$, 44 (18), 43 (20) $[C_3H_7]^+$, 41 (15).

3.3.6. 2-Methoxy-N-(2-diphenylphosphino-cyclohexylidene)aniline; dppCyHexMOA (5)

The synthesis of the ligand was performed following general procedure B described above starting from 1.00 g (4.91 mmol) substituted alkylidene aniline ***p-5***, 3.5 ml of a 1.6 M *n*-BuLi-solution and 1.10 g (4.99 mmol) $ClPPh_2$. The solid raw product was washed with *n*-pentane and dried in vacuo. Yield: 0.80 g (2.06 mmol, 42% of the theory) colourless powder. The compound is probably subject to a r.t. imine to enamine tautomer equilibrium ratio of about 3.5:1. Anal. Found: C, 77.55; H, 6.81; N, 3.71. Calc. for $C_{25}H_{26}NOP$: C, 77.50; H, 6.76; N, 3.62%. ^{1}H-NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 1.48–2.35$ (br m, 8H, CH_2), 3.54 (m, 1H PCH), 3.59, 3.69 (2*s, 3H, OCH_3), 6.10–7.58 (m, 14H, H_{arom}); $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75 MHz, only data for the main isomer are given) [ppm]: $\delta = 23.4$ (d, $J_{C,P} = 8.7$ Hz, CH_2), 27.9 (CH_2), 30.8 (d, $J_{C,P} = 12.6$ Hz, CH_2), 31.2 (d, $J_{C,P} = 3.9$ Hz, CH_2), 48.3 (d, $J_{C,P} = 13.0$ Hz, PCH), 55.4, 55.5 (OCH_3), 110.3–139.6 (CH_{arom}, C_{ipso}), 149.1 (NC_{ipso}), 175.7 (d, $J_{C,P} = 9.3$ Hz, C=N); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121 MHz): [ppm] $\delta = -10.17$ (s, ca. 0.8P, $Ph_2P\hat{}C{=}NAr$), −18.70 (s, ca. 0.2P, $Ph_2P\hat{}C{-}NHAr$); IR (KBr): [cm^{-1}] $\nu = 1660.6$ (s, C=N); MS: *m/z* ($I_{rel.}$/%) = 388 (9) $[M+1]^+$, 387 (31) $[M]^+$, 357 (24) $[M+1-OCH_3]^+$, 356 (100) $[M-OCH_3]^+$, 319 (20), 202 (8) $[M-PPh_2]^+$, 185 (7) $[PPh_2]^+$, 183 (13), 160 (10) $[CH_2CHCNAr]^+$, 133 (8) $[CNAr]^+$, 108 (10), 77 (15) $[C_6H_5]^+$, 44 (15), 31 (18) $[OCH_3]^+$.

3.3.7. 2,6-Diisopropyl-N-(2-diphenylphosphino-4-^{t}butyl-cyclohexylidene)aniline; dpptBuCyHexPA (6)

The synthesis of the ligand was performed following general procedure B described above starting from 4.36 g (13.90 mmol) substituted alkylidene aniline ***p-6***, 8.7 ml of a 1.6 M *n*-BuLi-solution and 3.05 g (13,82 mmol) $ClPPh_2$. The yellow raw product was treated with *n*-pentane and kept at −20 °C in order to induce crystallisation. Yield: 3.56 g (7.15 mmol, 52% of the theory) of colourless powder. Anal. Found: C, 82.10; H, 8.97; N, 2.88. Calc. for $C_{34}H_{44}NP$: C, 82.05; H, 8.91; N, 2.81%. Being the compound obtained as a mixture of diastereoisomers, an assignment of the NMR signals can only tentatively be given. ^{1}H-NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 0.65$, 0.68 (s, 9H, ^{t}Bu), 0.53, 0.88, 1.08, 1.11 (4*d, $J = 6.9$ Hz, 4*3H, CH_3^{iPr}), 1.15–2.50 (m, 8H), 2.80–2.92 (m, 1H), 3.19–3.33 (m, 0.5H), 3.90 (br m, 0.5H), 6.87–7.83 (m, 13H, H_{arom}); $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75 MHz): [ppm] $\delta = 22.8$, 23.3, 23.3, 23.4, 23.5, 23.5, 23.6 (CH_3^{iPr}), 27.2, 27.4 (CH_3^{tBu}), 27.4 (CH_2), 27.5, 27.7 (CH^{iPr}), 28.3, 29.2 (d), 31.6 (d), 31.8, 32.2 (CH_2), 34.7, 35.6 (CMe_3), 41.6 (d, $J_{C,P} = 8.8$ Hz, CH^tBu), 45.8 (d, $J_{C,P} = 8.5$ Hz, CH^tBu), 47.4 (d, $J_{C,P} = 15.0$ Hz, PCH), 48.1 (d, $J_{C,P} = 7.8$ Hz, PCH), 122.4–134.7 (CH_{arom}), 136.0–139.2 (C_{ipso}), 145.5, 145.6 (NC_{ipso}), 172.5 (d, $J_{C,P} = 6.6$ Hz, C=N), 174.6 (d, $J_{C,P} = 13.7$ Hz, C=N); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121 MHz): [ppm] $\delta = -8.35$ (s, ca. 0.7P), −15.46 (s, ca. 0.3P); IR (KBr): [cm^{-1}] $\nu = 1658.3$ (s, C=N); MS: *m/z* ($I_{rel.}$/%) = 498 (1) $[M+1]^+$, 497 (4) $[M]^+$, 482 (5) $[M-CH_3]^+$, 455 (31) $[M+1-C_3H_7]^+$, 454 (100) $[M-C_3H_7]^+$, 312 (10) $[M-PPh_2]^+$, 296 (10), 254 (10), 214 (23) $[CH_2CHCNAr]^+$, 201 (10), 186 (15), 185 (14) $[PPh_2]^+$, 183 (17), 108 (12), 91 (12) $[C_7H_7]^+$, 77 (11) $[C_6H_5]^+$, 57 (37) $[C_4H_9]^+$, 43 (42) $[C_3H_7]^+$, 41 (52) $[C_3H_5]^+$, 29 (27) $[C_2H_5]^+$.

3.3.8. 2,6-Diisopropyl-N-(2-diphenylphosphino-cycloheptylidene)aniline; dppCyHeptPA (7)

The synthesis of the ligand was performed following general procedure B starting from 5.08 g (18.71 mmol) substituted alkylidene aniline ***p-7***, 11.4 ml of a 1.6 M *n*-BuLi-solution and 4.05 g (18.36 mmol) $ClPPh_2$. The product precipitates as a solid and is recrystallised from *n*-pentane. Yield: 5.50 g (12.07 mmol, 66%) of colourless powder. Anal. Found: C, 81.64; H, 8.40; N, 3.00. Calc. for $C_{31}H_{38}NP$: C, 81.72; H, 8.41; N, 3.07%. ^{1}H-NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 0.69$, 0.85, 0.90, 1.01

(4*d, $J = 6.9$ Hz, 4*3H, CH_3^{iPr}), 1.23–1.80 (m, 8H, CH_2), 2.13–2.20 (m, 2H, CH_2), 2.20 (hept., $J = 6.9$ Hz, 1H, CH^{iPr}), 2.51 (hept., $J = 6.9$ Hz, 1H, CH^{iPr}), 3.71 (m, 1H, PCH), 6.86–7.65 (m, 13H, H_{arom}); $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75 MHz): [ppm] $\delta = 22.6$, 22.8, 23.8, 23.9 (CH_3^{iPr}), 24.4 (CH_2), 27.5, 27.7 (CH^{iPr}), 28.9 (CH_2), 29.5 (d, $J_{C,P} = 9.5$ Hz, CH_2), 30.4 (d, $J_{C,P} = 13.6$ Hz, CH_2), 34.0 (CH_2), 47.2 (d, $J_{C,P} = 9.8$ Hz, PCH), 122.7–134.4 (CH_{arom}), 135.5, 136.6 ($^iPrC_{ipso}$), 138.1 (d, $J_{C,P} = 14.4$ Hz, PC_{ipso}), 138.5 (d, $J_{C,P} = 17.4$ Hz, PC_{ipso}), 145.5 (NC_{ipso}), 175.9 (d, $J_{C,P} = 8.7$ Hz, C=N); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121 MHz): [ppm] $\delta = -10.91$(s); IR (KBr): [cm^{-1}] $\nu = 1637.2$ (s, C=N); MS: m/z ($I_{rel.}$/%) = 456 (1) $[M+1]^+$, 455 (5) $[M]^+$, 413 (26) $[M+1-C_3H_7]^+$, 412 (100) $[M-C_3H_7]^+$, 378 (4) $[M-Ph]^+$, 270 (26) $[M-PPh_2]^+$, 269 (26) $[M-CNAr+1]^+$, 254 (13) $[(CH_2)_4CHPPh_2]^+$, 226 (20) $[(CH_2)_2CHPPh_2]^+$, 186 (17) $[M-C_3H_7-(CH_2)_2CHPPh_2]^+$, 183 (12), 108 (9), 91 (11) $[C_7H_7]^+$, 43 (20) $[C_3H_7]^+$, 41 (18) $[C_3H_5]^+$.

3.3.9. 2,6-Diisopropyl-N-(1-n-propyl-2-diphenylphosphino-butylidene)aniline; dppHeptPA (**8**)

The synthesis of the ligand was performed following general procedure B starting from 5.08 g (18.57 mmol) substituted alkylidene aniline ***p-8***, 11.4 ml of a 1.6 M *n*-BuLi-solution and 4.05 g (18.36 mmol) $ClPPh_2$. Recrystallised from *n*-pentane. Yield: 5.19 g (11.33 mmol, 62%) colourless powder. Anal. Found: C, 81.46; H, 8.85; N, 3.12. Calc. for $C_{31}H_{40}NP$: C, 81.36; H, 8.81; N, 3.06%. ^1H-NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 0.69$ (t, $J = 7.2$ Hz, 3H, CH_3), 0.83, 0.88 (2*d, $J = 6.9$ Hz, 2*3H, CH_3^{iPr}), 0.95 (t, $J = 7.2$ Hz, 3H, CH_3), 1.00, 1.01 (2*d, $J = 6.9$ Hz, 2*3H, CH_3^{iPr}), 1.25–2.15 (m, 6H, CH_2), 2.37 (hept., $J = 6.9$ Hz, 1H, CH^{iPr}), 2.61 (hept., $J = 6.9$ Hz, 1H, CH^{iPr}), 3.45 (m, 1H, PCH), 6.87–7.64 (m, 13H, H_{arom}); $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75 MHz): [ppm] $\delta = 13.9$ (d, $J_{C,P} = 8.8$ Hz, CH_3), 14.6 (CH_3), 19.3 (CH_2), 22.6, 22.7, 23.6, 24.1 (CH_3^{iPr}), 23.9 (CH_2), 27.4, 27.8 (CH^{iPr}), 37.2 (d, $J_{C,P} = 3.0$ Hz, CH_2), 47.8 (d, $J_{C,P} = 15.0$ Hz, PCH), 122.5–133.8 (CH_{arom}), 136.0, 136.2 ($^iPrC_{ipso}$), 137.6 (d, $J_{C,P} = 15.5$ Hz, PC_{ipso}), 137.7 (d, $J_{C,P} = 17.4$ Hz, PC_{ipso}), 145.7 (NC_{ipso}), 174.4 (d, $J_{C,P} = 8.7$ Hz, C=N); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121 MHz): [ppm] $\delta = -2.95$ (s); IR (KBr): [cm^{-1}] $\nu = 1634.0$ (s, C=N); MS: m/z ($I_{rel.}$/%) = 458 (1) $[M+1]^+$, 457 (5) $[M]^+$, 415 (8) $[M+1-C_3H_7]^+$, 414 (37) $[M-C_3H_7]^+$, 272 (19) $[M-PPh_2]^+$, 230 (100) $[H_3C(CH_2)_2CNAr]^+$, 228 (37) $[H_3CCH_2CHPPh_2+1]^+$, 187 (14) $[H_3C(CH_2)_2CNAr-C_3H_7]^+$, 185 (10) $[PPh_2]^+$, 91 (18) $[C_7H_7]^+$, 55 (11) $[C_4H_7]^+$, 43 (40) $[C_3H_7]^+$, 41 (20) $[C_3H_5]^+$.

3.4. Synthesis of neutral palladium complexes

3.4.1. General procedure C

To a solution of 1.00 mmol palladium precursor in 5 ml CH_2Cl_2 kept under vigorous stirring, a solution of 1.00 equivalent of ligand in 7 ml of the same solvent is added dropwise at r.t. The solution is stirred for 30 min, then the solvent is reduced to 2 ml in vacuo and the product is precipitated by adding 20 ml *n*-pentane. The solid is filtered, washed with 3×10 ml pentane and dried. Complexes are obtained in nearly quantitative yields.

3.4.2. [{2,6-Dimethyl-N-(2-diphenylphosphino-cyclopentylidene)aniline-κ^2-P,N} (chloro)(methyl)-palladium(II)]; (dppCyPentMA)Pd(CH_3)Cl (**9**)

Scale: 262.3 mg (0,989 mmol) (cod)Pd(CH_3)Cl; 367.5 mg (0.989 mmol) (**1**); Yield: 496.6 mg (0.94 mmol, 95%) white solid. Anal. Found: C, 59.04; H, 5.50; N, 2.55. Calc. for $C_{26}H_{29}ClNPPd$: C, 59.11; H, 5.53; N, 2.65%.

^1H-NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 0.55$ (d, $J_{H,P} = 3.3$ Hz, 3H, $PdCH_3$), 1.51–1.68 (m, 2H, CH_2), 1.88–2.09 (m, 4H, CH_2), 2.11 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 4.14 (m, 1H, PCH), 6.88–7.94 (m, 13H, H_{arom}); $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75 MHz): [ppm] $\delta = -3.5$ ($PdCH_3$), 18.4, 19.0 (CH_3), 25.9 (d, $J_{C,P} = 7.1$ Hz, CH_2), 26.8 (d, $J_{C,P} = 8.4$ Hz, CH_2), 30.1 (d, $J_{C,P} = 6.6$ Hz, CH_2), 56.6 (d, $J_{C,P} = 26.1$ Hz, PCH), 125.6–136.6 (CH_{arom}, C_{ipso}), 146.1 (NC_{ipso}), 191.3 (d, $J_{C,P} = 10.4$ Hz, C=N); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121 MHz): [ppm] $\delta = 43.17$ (s); IR (KBr): [cm^{-1}] $\nu = 1645.2$ (s, C=N); SIMS (NBA), cation: m/z ($I_{rel.}$ (%)) = 514 (15) $[(P\wedge N)Pd(Cl)]^+$, 492 (42) $[(P\wedge N)Pd(CH_3)]^+$, 477 (9) $[(P\wedge N)Pd]^+$, 291 (7) $[PdPPh_2]^+$, 186 (100) $[(P\wedge N)-PPh_2$ or $PPh_2+1]^+$; SIMS (NBA), anion: m/z ($I_{rel.}$ (%)) = 528 (100) $[M-1]^-$, 341 (9) $[Cl+2NBA]^-$, 188 (49) $[Cl+NBA]^-$.

3.4.3. [{2,6-Diisopropyl-N-(2-diphenylphosphino-cyclopentylidene)aniline-κ^2-P,N} (chloro)(methyl)-palladium(II)]; (dppCyPentPA)Pd(CH_3)Cl (**12**)

Scale: 527.5 mg (1.990 mmol) (cod)Pd(CH_3)Cl; 850.9 mg (1.990 mmol) (**2**); Yield: 1128.2 mg (1.930 mmol, 97%) white solid. Anal. Found: C, 61.78; H, 6.40; N, 2.45. Calc. for $C_{30}H_{37}ClNPPd$: C, 61.65; H, 6.38; N, 2.40%.

^1H-NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 0.57$ (d, $J_{H,P} = 3.3$ Hz, 3H, $PdCH_3$), 0.90, 1.03, 1.32, 1.44 (4*d, $J = 6.9$ Hz, 4*3H, CH_3^{iPr}), 1.54–1.66 (m, 2H, CH_2), 1.88–2.12 (m, 4H, CH_2), 2.94 (hept., $J = 6.9$ Hz, 2H, CH^{iPr}), 4.18 (m, 1H, PCH), 7.04–7.96 (m, 13H, H_{arom}); $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75 MHz): [ppm] $\delta = -3.6$ (d, $J_{C,P} = 2.0$ Hz, $PdCH_3$), 23.3, 23.9, 24.0, 24.8 (CH_3^{iPr}), 25.7 (d, $J_{C,P} = 7.1$ Hz, CH_2), 26.9 (d, $J_{C,P} = 8.2$ Hz, CH_2), 28.1, 28.5 (CH^{iPr}), 31.2 (d, $J_{C,P} = 6.5$ Hz, CH_2), 56.2 (d, $J_{C,P} = 25.5$ Hz, PCH), 123.3–138.7 (CH_{arom},

C_{ipso}), 143.4 (NC_{ipso}), 191.7 (d, $J_{C,P} = 10.1$ Hz, C=N); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121 MHz): [ppm] $\delta = 42.70$ (s); IR (KBr): [cm^{-1}] $\nu = 1648.8$ (s, C=N); SIMS (NBA), cation: *m/z* ($I_{rel.}$ (%)) = 570 (27) $[(P\wedge N)Pd(Cl)]^+$, 548 (30) $[(P\wedge N)Pd(CH_3)]^+$, 533 (17) $[(P\wedge N)Pd]^+$, 346 (63) $[C_{17}H_{22}NPd]^+$, 291 (11) $[PdPPh_2]^+$, 242 (100) $[(P\wedge N)-PPh_2]^+$, 240 (87) $[C_{17}H_{22}N]^+$, 238 (20), 226 (16) $[(CH_2)_2CHPPh_2]^+$, 224 (11), 215 (10), 201 (8) $[CH_2CHNAr]^+$, 198 (11) $[CHPPh_2]^+$, 183 (13) $[CNAr]^+$; SIMS (NBA), anion: *m/z* ($I_{rel.}$ (%)) = 584 (100) $[M-1]^-$, 341 (5) $[Cl+2NBA]^-$, 188 (37) $[Cl+NBA]^-$.

3.4.4. [{2,6-Dimethyl-N-(2-diphenylphosphino-cyclohexylidene)aniline-κ^2-P,N}(chloro)(methyl)-palladium(II)]; (dppCyHexMA)Pd(CH_3)Cl (**15**)

Scale: 290.0 mg (1.094 mmol) (cod)Pd(CH_3)Cl; 421.7 mg (1.094 mmol) (**3**); Yield: 581.7 mg (1.072 mmol, 98%) white solid. Anal. Found: C, 59.70; H, 5.74; N, 2.55. Calc. for $C_{27}H_{31}ClNPPd$: C, 59.79; H, 5.76; N, 2.58%.

^{1}H-NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 0.54$ (d, $J_{H,P} = 2.7$ Hz, 3H, $PdCH_3$), 1.20–1.52 (m, 3H, CH_2), 1.62–1.91 (m, 4H, CH_2), 1.94 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.30–2.38 (m, 1H, CH_2), 3.60 (m, 1H, PCH), 6.91–7.73 (m, 13H, H_{arom}); $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75 MHz): [ppm] $\delta = -3.9$ ($PdCH_3$), 18.3, 19.0 (CH_3), 26.0 (d, $J_{C,P} = 7.5$ Hz, CH_2), 26.1 (CH_2), 31.9 (d, $J_{C,P} = 3.1$ Hz, CH_2), 32.9 (d, $J_{C,P} = 6.2$ Hz, CH_2), 53.9 (d, $J_{C,P} = 27.8$ Hz, PCH), 125.4–135.4 (CH_{arom}, C_{ipso}), 145.2 (NC_{ipso}), 182.5 (d, $J_{C,P} = 7.5$ Hz, C=N); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121 MHz): [ppm] $\delta = 49.60$ (s); IR (KBr): [cm^{-1}] $\nu = 1615.3$ (s, C=N); SIMS (NBA), cation: *m/z* ($I_{rel.}$ (%)) = 528 (16) $[(P\wedge N)Pd(Cl)]^+$, 506 (23) $[(P\wedge N)Pd(CH_3)]^+$, 491 (4) $[(P\wedge N)Pd]^+$, 384 (2) $[(P\wedge N)-1]^+$, 306 (16), 291 (10) $[PdPPh_2]^+$, 214 (3), 200 (100) $[(P\wedge N)-PPh_2]^+$, 198 (12) $[CHPPh_2]^+$, 153 (26); SIMS (NBA), anion: *m/z* ($I_{rel.}$ (%)) = 542 (100) $[M-1]^-$, 341 (4) $[Cl+2NBA]^-$, 188 (43) $[Cl+NBA]^-$, 152 (9).

3.4.5. [{2,6-Diisopropyl-N-(2-diphenylphosphino-hexylidene)aniline-κ^2-P,N}(chloro)(methyl)-palladium(II)]; (dppCyHexPA)Pd(CH_3)Cl (**18**)

Scale: 224.6 mg (0.847 mmol) (cod)Pd(CH_3)Cl; 373.7 mg (0.846 mmol) (**4**); Yield: 479.8 mg (0.802 mmol, 95%) white solid. Anal. Found: C, 62.34; H, 6.62; N, 2.41. Calc. for $C_{31}H_{39}ClNPPd$: C, 62.21; H, 6.57; N, 2.34%.

^{1}H-NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 0.54$ (d, $J_{H,P} = 2.7$ Hz, 3H, $PdCH_3$), 0.97, 1.03 (2*d, $J = 6.9$ Hz, 2*3H, CH_3^{iPr}), 1.16–1.27 (m, 1H, CH_2), 1.27, 1.44 (2*d, $J = 6.9$ Hz, 2*3H, CH_3^{iPr}), 1.32–1.53 (br m, 2H, CH_2), 1.68–1.95 (m, 4H, CH_2), 2.41–2.49 (m, 1H, CH_2), 2.67, 3.00 (2*hept., $J = 6.9$ Hz, 2*1H, CH^{iPr}), 3.60 (m, 1H, PCH), 7.05–7.79 (m, 13H, H_{arom}); $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75 MHz): [ppm] $\delta = -3.9$ ($PdCH_3$), 23.6, 23.8, 24.0, 24.0 (CH_3^{iPr}), 25.0 (CH_2), 25.7 (d, $J_{C,P} = 7.1$ Hz, CH_2), 28.1, 28.5 (CH^{iPr}), 30.8 (d, $J_{C,P} = 4.2$ Hz, CH_2), 33.7 (d, $J_{C,P} = 6.2$ Hz, CH_2), 53.6 (d, $J_{C,P} = 26.9$ Hz, PCH), 123.0–138.6 (CH_{arom}, C_{ipso}), 142.5 (NC_{ipso}), 181.7 (d, $J_{C,P} = 7.5$ Hz, C=N); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121 MHz): [ppm] $\delta = 49.78$ (s); IR (KBr): [cm^{-1}] $\nu = 1604.8$ (s, C=N); SIMS (NBA), cation: *m/z* ($I_{rel.}$ (%)) = 584 (37) $[(P\wedge N)Pd(Cl)]^+$, 562 (42) $[(P\wedge N)Pd(CH_3)]^+$, 547 (20) $[(P\wedge N)Pd]^+$, 398 (2) $[(P\wedge N)-C_3H_7]^+$, 360 (62) $[(CH_2)_4CHPPh_2Pd]^+$, 291 (13) $[PdPPh_2]^+$, 256 (100) $[(P\wedge N)-PPh_2]^+$, 254 (69) $[(CH_2)_4CHPPh_2]^+$, 240 (9) $[(CH_2)_3CHPPh_2]^+$, 212 (12) $[CH_2CHPPh_2]^+$, 186 (5) $[(P\wedge N)-C_3H_7\_CH_2CHPPh_2]^+$; SIMS (NBA), anion: *m/z* ($I_{rel.}$ (%)) = 598 (100) $[M-1]^-$, 188 (25) $[Cl+NBA]^-$.

3.4.6. [{2-Methoxy-N-(2-diphenylphosphino-cyclohexylidene)aniline-κ^2-P,N}(chloro)(methyl)-palladium(II)]; (dppCyHexMOA)Pd(CH_3)Cl (**21**)

Scale: 113.9 mg (0.430 mmol) (cod)Pd(CH_3)Cl; 166.3 mg (0.429 mmol) (**5**); yield: 221.5 mg (0.407 mmol, 95%) white solid; Anal. Found: C, 57.40; H, 5.42; N, 2.63. Calc. for $C_{26}H_{29}ClNOPPd$: C, 57.37; H, 5.37; N, 2.57%.

The product seems to be a mixture of diastereomers or rotamers in the ratio 1:1.

^{1}H-NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 0.55$, 0.56 (2*d, $J_{H,P} = 2.7$ Hz, 3H, $PdCH_3$), 1.33–2.10 (br m, 7H, CH_2), 2.50 (m, 1H, CH_2), 3.53 (m, 1H, PCH), 3.70, 3.80 (2*s, 3H, OCH_3), 6.71–7.76 (m, 14H, H_{arom}); $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75 MHz): [ppm] $\delta = -4.6$, -4.6 (2*s, $PdCH_3$), 25.6–33.8 (CH_2), 53.5 (d, $J_{C,P} = 28.2$ Hz, PCH), 54.0 (d, $J_{C,P} = 28.6$ Hz, PCH), 55.9, 56.2 (2*s, OCH_3), 111.5–136.3 (CH_{arom}, C_{ipso}), 149.9, 150.0 (NC_{ipso}), 183.0 (br, C=N), 183.8 (d, $J_{C,P} = 6.9$ Hz, C=N); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121 MHz): [ppm] $\delta = 50.22$ (s, 0.5P), 50.56 (s, 0.5P); IR (KBr): [cm^{-1}] $\nu = 1618.0$ (m, C=N); SIMS (NBA), cation: *m/z* ($I_{rel.}$ (%)) = 530 (15) $[(P\wedge N)Pd(Cl)]^+$, 508 (43) $[(P\wedge N)Pd(CH_3)]^+$, 493 (3) $[(P\wedge N)Pd]^+$, 291 (5) $[PdPPh_2]^+$, 202 (100) $[(P\wedge N)-PPh_2]^+$, 183 (4), 133 (4) $[CNAr]^+$; SIMS (NBA), anion: *m/z* ($I_{rel.}$ (%)) = 544 (83) $[M-1]^-$, 528 (5) $[M-CH_3]^-$, 341 (14) $[Cl+2NBA]^-$, 188 (100) $[Cl+NBA]^-$.

3.4.7. [{2,6-Diisopropyl-N-(2-diphenylphosphino-4-tert-butyl-cyclohexylidene)aniline-κ^2-P,N}(chloro)(methyl)-palladium(II)]; (dpptBuCyHexPA)Pd(CH_3)Cl (**23**)

Scale: 401.2 mg (1.513 mmol) (cod)Pd(CH_3)Cl; 752.2 mg (1.511 mmol) (**6**); yield: 923.5 mg (1.411 mmol, 93%) white solid. Anal. Found: C, 64.30; H, 7.27; N, 2.21. Calc. for $C_{35}H_{47}ClNPPd$: C, 64.22; H, 7.24; N, 2.14%.

Being the compound obtained as a mixture of diastereoisomers in the approximate ratio of 3:1, an assignment of the NMR signals can only tentatively be given.

^{1}H-NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 0.54$, 0.55 (2*d, $J = 3.0$ Hz, 3H, $PdCH_3$), 0.66, 0.68 (2*s, 9H, CH_3^{tBu}), 0.96–1.46 (8*d, $J = 6.9$ Hz, 4*3H, CH_3^{iPr}),

1.04–1.37 (br m, 2H, CH_2), 1.57–2.85 (br m, 5H, CH, CH_2), 2.64, 2.91 (2*hept., $J = 6.9$ Hz, 2*1H, CH^{iPr}), 3.63, 3.81 (2*m, 1H, PCH), 7.05–7.85 (m, 13H, H_{arom}); $^{13}C\{^1H\}$-NMR [selected signals] ($CDCl_3$, 75 MHz): [ppm] $\delta = -3.9$ (s, $PdCH_3$), 21.7 (CH_2), 23.5, 23.6, 23.7, 23.8, 23.9, 24.0, 24.7 (CH_3^{iPr}), 25.1 (d), 26.0 (CH_2), 26.7, 27.2 (CH_3^{tBu}), 28.1, 28.2, 28.5, 28.6 (CH^{iPr}), 31.6 (d), 31.8 (d), 33.1 (d) (CH_2), 32.5, 34.4 (CMe_3), 42.1 (d, $J_{C,P} = 4.9$ Hz, CH^tBu), 47.4 (d, $J_{C,P} = 5.9$ Hz, CH^tBu), 49.2 (d, $J_{C,P} = 25.5$ Hz, PCH), 53.1 (d, $J_{C,P} = 26.0$ Hz, PCH), 123.0–138.7 (CH_{arom}, C_{ipso}), 142.4, 142.5 (NC_{ipso}), 181.9 (d, $J_{C,P} = 7.4$ Hz, C=N), 184.3 (d, $J_{C,P} = 6.9$ Hz, C=N); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121 MHz): [ppm] $\delta = 50.15$ (s, ca. 0.75P), 52.09 (s, ca. 0.25P); IR (KBr): [cm^{-1}] $\nu = 1616.2$ (s, C=N); SIMS (NBA), cation: m/z ($I_{rel.}$ (%)) = 640 (99) $[(P\wedge N)Pd(Cl)]^+$, 618 (73) $[(P\wedge N)Pd(CH_3)]^+$, 603 (40) $[(P\wedge N)Pd]^+$, 416 (70) $[310+Pd]^+$, 312 (87) $[(P\wedge N)–PPh_2]^+$, 310 (74) $[(P\wedge N)–CNAr]^+$, 308 (12), 291 (29) $[PdPPh_2]^+$, 256 (15), 254 (15), 252 (11), 238 (12), 236 (10), 214 (17) $[CH_2CHCNAr]^+$, 212 (19) $[CH_2CHPPh_2]^+$, 201 (19), 196 (12), 186 (29) $[CNAr-1]^+$, 183 (17), 133 (100); SIMS (NBA), anion: m/z ($I_{rel.}$ (%)) = 654 (100) $[M-1]^-$, 188 (25) $[Cl+NBA]^-$.

3.4.8. [{2,6-Diisopropyl-N-(2-diphenylphosphino-cycloheptylidene)aniline-κ²-P,N}(chloro)(methyl)-palladium(II)]; (dppCyHeptPA)Pd(CH₃)Cl (**26**)

Scale: 434.8 mg (1.640 mmol) (cod)Pd(CH_3)Cl; 747.6 mg (1.641 mmol) (**7**); Yield: 963.7 mg (1.573 mmol, 96%) white solid. Anal. Found: C, 62.83; H, 6.80; N, 2.35. Calc. for $C_{32}H_{41}ClNPPd$: C, 62.75; H, 6.75; N, 2.29%.

^{1}H-NMR (CD_2Cl_2, 300 MHz): [ppm] $\delta = 0.58$ (br s, 3H, $PdCH_3$), 0.69, 0.99, 1.00, 1.34 (4*d, $J = 6.9$ Hz, 4*3H, CH_3^{iPr}), 1.18–1.32 (br m, 2H, CH_2), 1.50–1.90 (m, 6H, CH_2), 2.05–2.25 (br m, 3H, CH_2, CH^{iPr}), 2.72 (hept., $J = 6.9$ Hz, 1H, CH^{iPr}), 3.88 (br m, 1H, PCH), 6.95–7.84 (m, 13H, H_{arom}); $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 75 MHz): [ppm] $\delta = -4.7$ ($PdCH_3$), 23.6, 24.6, 24.7, 24.8 (CH_3^{iPr}), 25.4, 28.3 (CH_2), 28.5, 28.5 (CH^{iPr}), 30.7 (CH_2), 30.9 (d, $J_{C,P} = 11.0$ Hz, CH_2), 35.7 (d, $J_{C,P} = 7.1$ Hz, CH_2), 123.9–139.3 (CH_{arom}, C_{ipso}), 143.2 (NC_{ipso}), 186.7 (d, $J_{C,P} = 6.3$ Hz, C=N); $^{31}P\{^1H\}$-NMR (CD_2Cl_2, 121 MHz): [ppm] $\delta = 51.73$ (s); IR (KBr): [cm^{-1}] $\nu = 1604.2$ (s, C=N); SIMS (NBA), cation: m/z ($I_{rel.}$ (%)) = 598 (23) $[(P\wedge N)Pd(Cl)]^+$, 576 (36) $[(P\wedge N)Pd(CH_3)]^+$, 560 (10) $[(P\wedge N)Pd-1]^+$, 374 (20) $[268+Pd]^+$, 270 (100) $[(P\wedge N)–PPh_2]^+$, 268 (58) $[(CH_2)_5CHPPh_2]^+$, 266 (11); SIMS (NBA), anion: m/z ($I_{rel.}$ (%)) = 612 (100) $[M-1]^-$, 459 (64), 352 (18), 341 (29) $[Cl+2NBA]^-$, 321 (13), 190 (17), 188 (86) $[Cl+NBA]^-$.

3.4.9. [{2,6-Diisopropyl-N-(1-n-propyl-2-diphenylphosphinobutylidene)aniline-κ²-P,N}(chloro)-(methyl)palladium(II)]; (dppHeptPA)Pd(CH₃)Cl (**29**)

Scale: 477.2 mg (1.800 mmol) (cod)Pd(CH_3)Cl; 823.8 mg (1.800 mmol) (**8**); yield: 1070.7 mg (1.742 mmol, 97%) white solid. Anal. Found: C, 62.51; H, 7.04; N, 2.31. Calc. for $C_{32}H_{43}ClNPPd$: C, 62.54; H, 7.05; N, 2.28%.

^{1}H-NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 0.55$ (d, $J = 6.9$ Hz, 3H, CH_3^{iPr}), 0.78 (d, $J_{H,P} = 2.4$ Hz, 3H, $PdCH_3$), 0.71, 0.73 (2*t, $J = 7.2$ Hz, 2*3H, CH_3), 1.01, 1.17, 1.35 (3*d, $J = 6.9$ Hz, 3*3H, CH_3^{iPr}), 1.40–2.08 (m, 6H, CH_2), 2.16, 2.67 (2*hept. , $J = 6.9$ Hz, 2*1H, CH^{iPr}), 3.65 (m, 1H, PCH), 6.93–7.95 (m, 13H, H_{arom}); $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75 MHz): [ppm] $\delta = -4.5$ ($PdCH_3$), 13.5 (d, $J_{C,P} = 6.7$ Hz, CH_3), 14.4 (CH_3), 19.8 (CH_2), 22.6, 24.2, 24.2, 25.0 (CH_3^{iPr}), 25.9 (d, $J_{C,P} = 5.6$ Hz, CH_2), 27.6, 28.2 (CH^{iPr}), 37.1 (d, $J_{C,P} = 5.5$ Hz, CH_2), 52.7 (d, $J_{C,P} = 28.6$ Hz, PCH), 123.2–138.6 (CH_{arom}, C_{ipso}), 142.0 (NC_{ipso}), 184.2 (d, $J_{C,P} = 6.7$ Hz, C=N); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121 MHz): [ppm] $\delta = 53.29$ (s); IR (KBr): [cm^{-1}] $\nu = 1599.5$ (s, C=N); SIMS (NBA), cation: m/z ($I_{rel.}$ (%)) = 600 (60) $[(P\wedge N)Pd(Cl)]^+$, 578 (67) $[(P\wedge N)Pd(CH_3)]^+$, 562 (19) $[(P\wedge N)Pd-1]^+$, 376 (83) $[270+Pd]^+$, 291 (14) $[PdPPh_2]^+$, 272 (100) $[(P\wedge N)–PPh_2]^+$, 270 (54) $[C_{19}H_{28}N]^+$, 230 (56) $[H_3C(CH_2)_2CNAr]^+$, 228 (90) $[H_3CCH_2CHPPh_2+1]^+$, 226 (26), 214 (24) $[CH_2CHPPh_2]^+$, 212 (14), 201 (11) $[CH_2CNAr]^+$, 186 (28) $[PPh_2+1]^+$, 183 (12), 172 (14), 133 (12); SIMS (NBA), Anion: m/z ($I_{rel.}$ (%)) = 614 (100) $[M-1]^-$, 598 (6) $[M-CH_3]^-$, 341 (5) $[Cl+2NBA]^-$, 188 (54) $[Cl+NBA]^-$.

3.5. Synthesis of cationic palladium complexes

3.5.1. General procedure D

0.7 mmol of the relevant (chloro)(methyl)palladium(II) complex $[(P\wedge N)Pd(CH_3)Cl]$ are dissolved in 4 ml CH_2Cl_2 and 0.4 ml MeCN. To this solution, kept under vigorous stirring, 1.02 equivalents of $AgSbF_6$ suspended in 4 ml CH_2Cl_2 are added at a temperature ranging from 0 to 20°C, causing the immediate precipitation of silver chloride. The suspension is stirred for 5 min, AgCl is filtered on Celite® and the clear solution concentrated to 1 ml. The product is obtained by adding 20 ml of *n*-pentane, isolated and dried in vacuo.

3.5.2. [(Acetonitrile){2,6-dimethyl-N-(2-diphenylphosphino-cyclopentylidene)aniline-κ²-P,N}(methyl)palladium(II)]hexafluoroantimonate; [(dppCyPentMA)Pd(CH₃)(NCCH₃)]SbF₆ (**10**)

Scale: 273.2 mg (0.517 mmol) (**9**); 174.9 mg (0.509 mmol) $AgSbF_6$; Yield: 351.0 mg (0.456 mmol, 90%) white powder. Anal. Found: C, 43.74; H, 4.20; N, 3.68.

Calc. for $C_{28}H_{32}F_6N_2PPdSb$: C, 43.69; H, 4.19; N, 3.64%.

^{1}H-NMR (CD_2Cl_2, 300 MHz): [ppm] $\delta = 0.34$ (d, $J_{H,P} = 1.8$ Hz, 3H, $PdCH_3$), 1.48–1.70 (m, 2H, CH_2), 1.73 (s, 3H, $NCCH_3$), 2.01–2.24 (br m, 4H, CH_2), 2.12, 2.16 (2*s, 2*3H, CH_3), 4.39 (m, 1H, PCH), 7.01–7.86 (m, 13H, H_{arom}); $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 75 MHz): [ppm] $\delta = -3.1$ ($PdCH_3$), 2.0 ($NCCH_3$), 18.2, 18.9 (CH_3), 26.6 (d, $J_{C,P} = 6.3$ Hz, CH_2), 27.8 (d, $J_{C,P} = 9.3$ Hz, CH_2), 30.6 (d, $J_{C,P} = 7.0$ Hz, CH_2), 58.5 (d, $J_{C,P} = 30.0$ Hz, PCH), 119.5 ($NCCH_3$), 124.5–137.0 (CH_{arom}, C_{ipso}), 145.5 (NC_{ipso}), 195.8 (d, $J_{C,P} = 9.0$ Hz, C=N); $^{31}P\{^1H\}$-NMR (CD_2Cl_2, 121 MHz): [ppm] $\delta = 44.51$ (s). IR (KBr): [cm^{-1}] $\nu = 1661.0$ (m, C=N), 2309.2, 2282.1 (w, C≡N); SIMS (DTE/DTT/Sul), cation: *m/z* ($I_{rel.}$ (%)) = 630 (15) $[(P\wedge N)Pd + DTE/DTT - 1]^+$, 492 (43) $[(P\wedge N)Pd(CH_3)]^+$, 477 (22) $[(P\wedge N)Pd]^+$, 372 (4) $[(P\wedge N)+1]^+$, 370 (6) $[(P\wedge N)-1]^+$, 291 (11) $[PdPPh_2]^+$, 186 (100) $[(P\wedge N)–PPh_2, PPh_2+1]^+$; SIMS (DTE/DTT/Sul), Anion: *m/z* ($I_{rel.}$ (%)) = 235 (100) $[SbF_6]^-$.

3.5.3. [(Acetonitrile){2,6-diisopropyl-N-(2-diphenylphosphino-cyclopentylidene)aniline-κ^2-P,N}(methyl)palladium(II)]hexafluoroantimonate; [(dppCyPentPA)Pd(CH_3)($NCCH_3$)]SbF_6 (**13**)

Scale: 464.6 mg (0.795 mmol) (**12**); 276.7 mg (0.805 mmol) $AgSbF_6$; yield: 631.6 mg (0,765 mmol, 96%) white powder. Anal. Found: C, 46.53; H, 4.92; N, 3.30. Calc. for $C_{32}H_{40}F_6N_2PPdSb$: C, 46.54; H, 4.88; N, 3.39%.

^{1}H-NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 0.33$ (d, $J_{H,P} = 2.1$ Hz, 3H, $PdCH_3$), 0.95, 1.16, 1.21, 1.40 (4*d, $J = 6.9$ Hz, 4*3H, CH_3^{iPr}), 1.49–1.76 (m, 2H, CH_2), 1.71 (s, 3H, $NCCH_3$), 1.98–2.30 (m, 4H, CH_2), 2.89 (hept., $J = 6.9$ Hz, 1H, CH^{iPr}), 2.96 (hept., $J = 6.9$ Hz, 1H, CH^{iPr}), 4.67 (dt, $J_{H,H} = 7.8$ Hz, $J_{H,P} = 11.4$ Hz, 1H, PCH), 7.13–7.85 (m, 13H, H_{arom}); $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75 MHz): [ppm] $\delta = -3.2$ (d, $J_{C,P} = 2.1$ Hz, $PdCH_3$), 1.3 ($NCCH_3$), 23.5, 23.7, 23.8, 24.5 (CH_3^{iPr}), 25.9 (d, $J_{C,P} = 6.6$ Hz, CH_2), 27.0 (d, $J_{C,P} = 9.4$ Hz, CH_2), 28.2, 28.3 (CH^{iPr}), 30.9 (d, $J_{C,P} = 7.0$ Hz, CH_2), 57.1 (d, $J_{C,P} = 30.0$ Hz, PCH), 119.0 ($NCCH_3$), 124.9–138.6 (CH_{arom}, C_{ipso}), 142.2 (NC_{ipso}), 195.7 (d, $J_{C,P} = 8.7$ Hz, C=N); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121 MHz): [ppm] $\delta = 45.07$ (s); IR (KBr): [cm^{-1}] $\nu = 1653.4$ (s, C=N), 2317.6, 2289.7 (w, C≡N); SIMS (DTE/DTT/Sul), cation: *m/z* ($I_{rel.}$ (%)) = 686 (7) $[(P\wedge N)Pd + DTE/DTT - 1]^+$, 548 (37) $[(P\wedge N)Pd(CH_3)]^+$, 533 (22) $[(P\wedge N)Pd]^+$, 346 (12) $[C_{17}H_{22}NPd]^+$, 291 (4) $[PdPPh_2]^+$, 242 (58) $[(P\wedge N)–PPh_2]^+$, 240 (27) $[C_{17}H_{22}N]^+$, 238 (7), 226 (6) $[(CH_2)_2CHPPh_2]^+$, 147 (19), 109 (26), 97 (13), 95 (40), 93 (16), 83 (25), 81 (95), 69 (100), 67 (31); SIMS (DTE/DTT/Sul), Anion: *m/z* ($I_{rel.}$ (%)) = 235 (100) $[SbF_6]^-$.

3.5.4. [(Acetonitrile){2,6-dimethyl-N-(2-diphenylphosphino-cyclohexylidene)aniline-κ^2-P,N}(methyl)palladium(II)]hexafluoroantimonate; [(dppCyHexMA)Pd(CH_3)($NCCH_3$)]SbF_6 (**16**)

Scale: 354.9 mg (0,654 mmol) (**15**); 230.8 mg (0.672 mmol) $AgSbF_6$; yield: 474.7 mg (0.605 mmol, 92%) white solid. Anal. Found: C, 44.58; H, 4.42; N, 3.61. Calc. for $C_{29}H_{34}F_6N_2PPdSb$: C, 44.44; H, 4.37; N, 3.57%.

^{1}H-NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 0.32$ (d, $J_{H,P} = 1.8$ Hz, 3H, $PdCH_3$), 1.17–1.32 (m, 2H, CH_2), 1.60–1.83 (m, 4H, CH_2), 1.74 (s, 3H, $NCCH_3$), 2.01, 2.20 (2*s, 2*3H, CH_3), 2.16–2.40 (m, 2H, CH_2), 4.00 (m, 1H, PCH), 7.00–7.69 (m, 13H, H_{arom}); $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75 MHz): [ppm] $\delta = -3.2$ ($PdCH_3$), 1.3 ($NCCH_3$), 17.9, 18.5 (CH_3), 25.2 (d, $J_{C,P} = 8.3$ Hz, CH_2), 26.3 (CH_2), 32.3 (d, $J_{C,P} = 3.2$ Hz, CH_2), 32.6 (d, $J_{C,P} = 6.1$ Hz, CH_2), 53.8 (d, $J_{C,P} = 31.2$ Hz, PCH), 118.5 ($NCCH_3$), 124.4–135.6 (CH_{arom}, C_{ipso}), 144.6 (NC_{ipso}), 186.0 (d, $J_{C,P} = 5.3$ Hz, C=N); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121 MHz): [ppm] $\delta = 52.85$ (s); IR (KBr): [cm^{-1}] $\nu = 1622.7$ (m, C=N), 2318.2, 2289.6 (w, C≡N); SIMS (NBA), cation: *m/z* ($I_{rel.}$ (%)) = 506 (17) $[(P\wedge N)Pd(CH_3)]^+$, 491 (3) $[(P\wedge N)Pd]^+$, 384 (2) $[(P\wedge N)-1]^+$, 327 (4), 291 (12) $[PdPPh_2]^+$, 281 (7), 221 (6), 214 (5), 200 (100) $[(P\wedge N)–PPh_2]^+$, 198 (13) $[CHPPh_2]^+$, 147 (33); SIMS (NBA), anion: *m/z* ($I_{rel.}$ (%)) = 235 (100) $[SbF_6]^-$.

3.5.5. [(Acetonitrile){2,6-diisopropyl-N-(2-diphenylphosphino-cyclohexylidene)aniline-κ^2-P,N}(methyl)palladium(II)]hexafluoroantimonate; [(dppCyHexPA)Pd(CH_3)($NCCH_3$)]SbF_6 (**19**)

Scale: 447.3 mg (0.747 mmol) (**18**); 260.8 mg (0.759 mmol) $AgSbF_6$; yield: 612.8 mg (0.730 mmol, 98%) white powder. Anal. Found: C, 47.32; H, 5.10; N, 3.36. Calc. for $C_{33}H_{42}F_6N_2PPdSb$: C, 47.20; H, 5.04; N, 3.34%.

^{1}H-NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 0.29$ (d, $J_{H,P} = 1.5$ Hz, 3H, $PdCH_3$), 1.08, 1.09, 1.16 (3*d, $J = 6.9$ Hz, 3*3H, CH_3^{iPr}), 1.16–1.30 (m, 2H, CH_2), 1.39 (d, $J = 6.9$ Hz, 3H, CH_3^{iPr}), 1.69 (s, 3H, $NCCH_3$), 1.68–1.96 (m, 4H, CH_2), 2.20 (m, 1H, CH_2), 2.44 (m, 1H, CH_2), 2.63 (hept., $J = 6.9$ Hz, 1H, CH^{iPr}), 2.90 (hept., $J = 6.9$ Hz, 1H, CH^{iPr}), 4.07 (m, 1H, PCH), 7.13–7.71 (m, 13H, H_{arom}); $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75 MHz): [ppm] $\delta = -3.6$ ($PdCH_3$), 1.1 ($NCCH_3$), 23.4, 23.5, 23.7, 23.8 (CH_3^{iPr}), 24.8 (d, $J_{C,P} = 8.1$ Hz, CH_2), 25.3 (CH_2), 28.0, 28.3 (CH^{iPr}), 31.5 (d, $J_{C,P} = 3.5$ Hz, CH_2), 33.3 (d, $J_{C,P} = 5.9$ Hz, CH_2), 53.5 (d, $J_{C,P} = 30.7$ Hz, PCH), 118.8 ($NCCH_3$), 123.7–138.9 (CH_{arom}, C_{ipso}), 141.8 (NC_{ipso}), 185.5 (d, $J_{C,P} = 6.3$ Hz, C=N); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121 MHz): [ppm] $\delta = 53.41$ (s); IR (KBr): [cm^{-1}] $\nu = 1620.8$ (m, C=N), 2319.4, 2291.6 (w, C≡N); SIMS (DTE/DTT/Sul), cation: *m/z* ($I_{rel.}$ (%)) =

700 (16) $[(P\wedge N)Pd+DTE/DTT-1]^+$, 562 (32) $[(P\wedge N)Pd(CH_3)]^+$, 547 (22) $[(P\wedge N)Pd]^+$, 360 (28) $[(CH_2)_4CHPPh_2Pd]^+$, 291 (10) $[PdPPh_2]^+$, 256 (100) $[(P\wedge N)-PPh_2]^+$, 254 (36) $[(CH_2)_4CHPPh_2]^+$, 240 (10) $[(CH_2)_3CHPPh_2]^+$, 214 (16), 212 (11) $[CH_2CHPPh_2]^+$, 133 (67), 73 (41); SIMS (DTE/DTT/Sul), Anion: *m/z* ($I_{rel.}$ (%)) = 235 (100) $[SbF_6]^-$.

3.5.6. [(Acetonitrile){2-methoxy-N-(2-diphenylphosphino-cyclohexylidene)aniline-κ²-P,N}(methyl)palladium(II)]hexafluoroantimonate; [(dppCyHexMOA)Pd(CH₃)(NCCH₃)]SbF₆ (**22**)

Scale: 142.8 mg (0.262 mmol) (**21**); 93.8 mg (0.273 mmol) $AgSbF_6$; Yield: 190.0 mg (0.242 mmol, 92%) bright yellow powder. Anal. Found: C, 42.68; H, 4.05; N, 3.52. Calc. for $C_{28}H_{32}F_6N_2OPPdSb$: C, 42.80; H, 4.10; N, 3.56%.

^{1}H-NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 0.31$ (br s, 3H, $PdCH_3$), 1.20–1.79 (br m, 5H, CH_2), 1.84 (s, 3H, $NCCH_3$), 2.20 (m, 1H, CH_2), 2.46 (m, 2H, CH_2), 3.82 (s, 3H, OCH_3), 3.85 (m, 1H, PCH), 6.88–7.72 (m, 14H, H_{arom}); $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75 MHz): [ppm] $\delta = -4.2$ ($PdCH_3$), 1.6 ($NCCH_3$), 25.1 (d, $J_{C,P} = 7.$ Hz, CH_2), 27.8 (CH_2), 31.2 (br, CH_2), 33.2 (d, $J_{C,P} = 5.2$ Hz, CH_2), 53.7 (br, PCH), 55.9 (s, OCH_3), 118.7 ($NCCH_3$), 111.6–135.5 (CH_{arom}, C_{ipso}), 150.0 (NC_{ipso}), 182.4 (br, C=N); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121 MHz): [ppm] $\delta = 53.07$ (br s); IR (KBr): [cm^{-1}] $\nu = 1625.9$ (m, C=N), 2318.6, 2290.7 (w, C≡N); SIMS (DTE/DTT/Sul), cation: *m/z* ($I_{rel.}$ (%)) = 646 (5) $[(P\wedge N)Pd+DTE/DTT-1]^+$, 508 (45) $[(P\wedge N)Pd(CH_3)]^+$, 493 (8) $[(P\wedge N)Pd]^+$, 388 (5), 291 (4) $[PdPPh_2]^+$, 202 (100) $[(P\wedge N)-PPh_2]^+$, 185 (4), 183 (4); SIMS (DTE/DTT/Sul), anion: *m/z* ($I_{rel.}$ (%)) = 235 (100) $[SbF_6]^-$, 119 (11).

3.5.7. [(Acetonitrile){2,6-diisopropyl-N-(4-tert.-butyl-2-diphenylphosphino-cyclohexylidene)-aniline-κ²-P,N}(methyl)palladium(II)]hexafluoroantimonate; [(dpptBuCyHexPA)Pd(CH₃)(NCCH₃)]SbF₆ (**24**)

Scale: 466.7 mg (0.713 mmol) (**23**); 251.2 mg (0.731 mmol) $AgSbF_6$; yield: 596.4 mg (0.667 mmol, 93%) white powder. Anal. Found: C, 49.68; H, 5.67; N, 3.18. Calc. for $C_{37}H_{50}F_6N_2PPdSb$: C, 49.60; H, 5.62; N, 3.13%.

Being the compound obtained as a mixture of diastereoisomers in the approximate ratio of 3:1, an assignment of the NMR signals can only tentatively be given.

^{1}H-NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 0.31$, 0.34 (2*s, 3H, $PdCH_3$), 0.63, 0.65 (2*s, 9H, CH_3^{tBu}), 0.78–0.83 (m, 2H, CH_2), 1.03, 1.08, 1.10, 1.16 (4*d, $J = 6.9$ Hz, 4*3H, CH_3^{iPr}), 1.77 (s, 3H, $NCCH_3$), 1.50–2.56 (br m, 5H, CH, CH_2), 2.64 (br m, 1H, CH^{iPr}), 2.91 (br m, 1H, CH^{iPr}), 4.18 (m, 1H, PCH), 7.15–7.74 (m, 13H, H_{arom}); $^{13}C\{^1H\}$-NMR [selected signals] ($CDCl_3$, 75 MHz): [ppm] $\delta = -3.6$, −3.5 (2*s, $PdCH_3$), 1.2 ($NCCH_3$), 22.0 (br, CH_2), 23.4, 23.5, 23.8, 23.9 (CH_3^{iPr}), 26.3 (br, CH_2), 26.7, 27.1 (CH_3^{tBu}), 28.1, 28.3 (CH^{iPr}), 32.7 (br, CH_2), 32.3, 34.1 (CMe_3), 42.6 (d, $J_{C,P} = 5.1$ Hz, CH^tBu), 45.8 (d, $J_{C,P} = 6.9$ Hz, CH^tBu), 50.2 (d, $J_{C,P} = 30.0$ Hz, PCH), 53.0 (d, $J_{C,P} = 30.1$ Hz, PCH), 118.6 (br, $NCCH_3$), 123.7–139.0 (CH_{arom}, C_{ipso}), 141.6, 141.9 (NC_{ipso}), 185.8 (d, $J_{C,P} = 5.3$ Hz, C=N), 188.2 (d, $J_{C,P} = 5.4$ Hz, C=N); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121 MHz): [ppm] $\delta = 53.66$ (s, ca. 0.75P), 54.00 (s, ca. 0.25P); IR (KBr): [cm^{-1}] $\nu = 1628.3$ (s, C=N), 2319.7, 2292.4 (w, C≡N); SIMS (DTE/DTT/Sul), cation: *m/z* ($I_{rel.}$ (%)) = 756 (43) $[(P\wedge N)Pd+DTE/DTT-1]^+$, 618 (80) $[(P\wedge N)Pd(CH_3)]^+$, 603 (43) $[(P\wedge N)Pd]^+$, 416 (55) $[310+Pd]^+$, 312 (100) $[(P\wedge N)-PPh_2]^+$, 310 (53) $[(P\wedge N)-CNAr]^+$, 291 (20) $[PdPPh_2]^+$, 256 (13), 254 (12), 214 (27) $[CH_2CHCNAr]^+$, 212 (16) $[CH_2CHPPh_2]^+$, 201 (12), 186 (20) [CNAr-1, $Ph_2P+1]^+$, 183 (17), 133 (94); SIMS (DTE/DTT/Sul), Anion: *m/z* ($I_{rel.}$ (%)) = 235 (100) $[SbF_6]^-$.

3.5.8. [(Acetonitrile){2,6-diisopropyl-N-(2-diphenylphosphino-cycloheptylidene)aniline-κ²-P,N}(methyl)palladium(II)]hexafluoroantimonate; [(dppCyHeptPA)Pd(CH₃)(NCCH₃)]SbF₆ (**27**)

Scale: 474.0 mg (0.774 mmol) (**26**); 275.0 mg (0.800 mmol) $AgSbF_6$; yield: 640.0 mg (0.750 mmol, 97%) white powder. Anal. Found: C, 47.90; H, 5.23; N, 3.34. Calc. for $C_{34}H_{44}F_6N_2PPdSb$: C, 47.83; H, 5.19; N, 3.28%.

^{1}H-NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 0.50$ (d, $J_{H,P} = 1.2$ Hz, 3H, $PdCH_3$), 0.81, 0.94, 1.11, 1.27 (4*d, $J = 6.9$ Hz, 4*3H, CH_3^{iPr}), 1.20–1.53 (br m, 2H, CH_2), 1.70 (s, 3H, $NCCH_3$), 1.68–1.95 (m, 6H, CH_2), 2.20 (hept., $J = 6.9$ Hz, 1H, CH^{iPr}), 2.31 (t, $J = 6.6$ Hz, 2H, CH_2), 2.74 (hept., $J = 6.9$ Hz, 1H, CH^{iPr}), 4.16 (m, 1H, PCH), 7.06–7.74 (m, 13H, H_{arom}); $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75 MHz): [ppm] $\delta = -4.1$ ($PdCH_3$), 1.3 ($NCCH_3$), 23.3, 23.8, 23.8, 24.3 (CH_3^{iPr}), 24.2, 27.6 (CH_2), 27.9, 28.0 (CH^{iPr}), 29.7 (d, $J_{C,P} = 11.1$ Hz, CH_2), 30.2 (CH_2), 35.1 (d, $J_{C,P} = 3.5$ Hz, CH_2), 53.9 (d, $J_{C,P} = 31.0$ Hz, PCH), 118.8 ($NCCH_3$), 124.0–139.0 (CH_{arom}, C_{ipso}), 141.7 (NC_{ipso}), 188.8 (d, $J_{C,P} = 5.0$ Hz, C=N); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121 MHz): [ppm] $\delta = 54.43$ (s); IR (KBr): [cm^{-1}] $\nu = 1606.9$ (m, C=N), 2319.0, 2290.8 (w, C≡N); SIMS (DTE/DTT/Sul), cation: *m/z* ($I_{rel.}$ (%)) = 714 (22) $[(P\wedge N)Pd+DTE/DTT-1]^+$, 576 (67) $[(P\wedge N)Pd(CH_3)]^+$, 561 (23) $[(P\wedge N)Pd]^+$, 387 (18), 374 (30) $[(CH_2)_5CHPPh_2+Pd]^+$, 291 (12) $[PdPPh_2]^+$, 270 (100) $[(P\wedge N)-PPh_2]^+$, 268 (41) $[(CH_2)_5CHPPh_2]^+$, 226 (10) $[(CH_2)_2CHPPh_2]^+$, 147 (18), 133 (86), 119 (13), 85 (23), 73 (59); SIMS (DTE/DTT/Sul), Anion: *m/z* ($I_{rel.}$ (%)) = 235 (100) $[SbF_6]^-$.

*3.5.9. [(Acetonitrile){2,6-diisopropyl-N-(2-diphenylphosphino-1-n-propyl-butylidene)aniline-κ^2-P,N}(methyl)palladium(II)]hexafluoroantimonate; [(dppHeptPA)Pd(CH_3)($NCCH_3$)]SbF_6 (**30**)*

Scale: 513.4 mg (0.835 mmol) (**29**); 296.6 mg (0.863 mmol) $AgSbF_6$; yield: 683.1 mg (0.798 mmol, 96%) white powder. Anal. Found: C, 47.70; H, 5.38; N, 3.23. Calc. for $C_{34}H_{46}F_6N_2PPdSb$: C, 47.71; H, 5.42; N, 3.27%.

^{1}H-NMR ($CDCl_3$, 300 MHz): [ppm] $\delta = 0.60$ (br s, 3H, $PdCH_3$), 0.62 (d, $J = 6.9$ Hz, 3H, CH_3^{iPr}), 0.76, 0.77 (2*t, $J = 7.2$ Hz, 2*3H, CH_3), 1.07, 1.10, 1.22 (3*d, $J = 6.9$ Hz, 3*3H, CH_3^{iPr}), 1.73 (br s, 3H, $NCCH_3$), 1.59–2.29 (m, 7H, CH_2, CH^{iPr}), 2.60 (hept., $J = 6.9$ Hz, 1H, CH^{iPr}), 3.98 (m, 1H, PCH), 7.07–7.62 (m, 13H, H_{arom}); $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75 MHz): [ppm] $\delta = -4.4$ ($PdCH_3$), 1.3 ($NCCH_3$), 12.9 (d, $J_{C,P} = 6.5$ Hz, CH_3), 14.3 (CH_3), 19.8 (CH_2), 22.8, 23.5, 23.5, 24.8 (CH_3^{iPr}), 26.2 (d, $J_{C,P} = 3.5$ Hz, CH_2), 27.7, 28.0 (CH^{iPr}), 37.0 (d, $J_{C,P} = 5.9$ Hz, CH_2), 53.4 (d, $J_{C,P} = 32.3$ Hz, PCH), 118.7 ($NCCH_3$), 123.4–138.9 (CH_{arom}, C_{ipso}), 141.5 (NC_{ipso}), 187.6 (d, $J_{C,P} = 5.0$ Hz, C=N); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 121 MHz): [ppm] $\delta = 55.72$ (s); IR (KBr): [cm^{-1}] $\nu = 1609.3$ (s, C=N), 2318.6, 2291.1 (w, C≡N); SIMS (DTE/DTT/Sul), cation: *m/z* ($I_{rel.}$ (%)) = 716 (43) $[(P\wedge N)Pd + DTE/DTT - 1]^+$, 578 (46) $[(P\wedge N)Pd(CH_3)]^+$, 564 (18) $[(P\wedge N)Pd + 1]^+$, 376 (40) $[C_{19}H_{28}N + Pd]^+$, 291 (9) $[PdPPh_2]^+$, 272 (100) $[(P\wedge N) - PPh_2]^+$, 270 (26) $[C_{19}H_{28}N]^+$, 230 (52) $[H_3C(CH_2)_2CNAr]^+$, 228 (45) $[H_3CCH_2CHPPh_2 + 1]^+$, 226 (12), 214 (14) $[CH_2CHPPh_2]^+$, 212 (8), 186 (16) $[PPh_2 + 1]^+$, 172 (8), 133 (18); SIMS (DTE/DTT/Sul), Anion: *m/z* ($I_{rel.}$ (%)) = 235 (100) $[SbF_6]^-$.

3.6. Synthesis of P^N nickel(II) bromide complexes

0.4 mmol of (1,2-dimethoxyethane)nickel(II)bromide are suspended in 4 ml CH_2Cl_2 at r.t. with the aid of an ultrasound bath and slowly reacted with a solution of 1.00 equivalent of ligand dissolved in 3 ml CH_2Cl_2. The suspension colour turns into red brown. It is vigorously stirred for 1 h and eventually filtered with Celite®. The filtrate is concentrated, washed with *n*-pentane and dried in vacuo. Yields are almost quantitative and the products can be crystallised from CH_2Cl_2. NMR measures could not be possible due to paramagnetism. IR characterisation was reported in the discussion (vide supra).

Elemental analyses: (**11**) Found: C, 50.95; H, 4.50; N, 2.39. Calc. for $C_{25}H_{26}Br_2NNiP$: C, 50.90; H, 4.44; N, 2.37%; (**14**) Found: C, 53.95; H, 5.38; N, 2.20. Calc. for $C_{29}H_{34}Br_2NNiP$: C, 53.91; H, 5.31; N, 2.17%; (**17**) Found: C, 51.80; H, 4.74; N, 2.38. Calc. for $C_{26}H_{28}Br_2NNiP$: C, 51.70; H, 4.67; N, 2.32%; (**20**) Found: C, 54.60; H, 5.51; N, 2.10. Calc. for $C_{30}H_{36}Br_2NNiP$: C, 54.59; H, 5.50; N, 2.12%; (**25**) Found: C, 57.12; H, 6.20; N, 2.00. Calc. for $C_{34}H_{44}Br_2NNiP$: C, 57.02; H, 6.19; N, 1.96%; (**28**) Found: C, 55.15; H, 5.71; N, 2.08. Calc. for $C_{31}H_{38}Br_2NNiP$: C, 55.23; H, 5.68; N, 2.08%; (**31**) Found: C, 55.10; H, 5.91; N, 2.12. Calc. for $C_{31}H_{40}Br_2NNiP$: C, 55.07; H, 5.96; N, 2.07%.

3.7. Typical procedure for palladium catalysed alkene oligomerisation

The ethylene oligomerisation tests were performed under a constant ethylene pressure in 75 ml steel autoclaves equipped with glass inlets and magnetic stirring bar. A Schlenk tube was added of 0.05 mmol catalyst and 5 ml solvent and the obtained solution transferred into the autoclave, washing the tube with other 3 × 5 ml solvent. The autoclave was then set to the desired constant ethylene pressure, temperature and stirring rate (set to 1000 rpm). After reaction time (typically 2 h) the autoclave was cooled in an ice bath and opened. The obtained butenes were collected at −78 °C and their quantity determined by weighing. The liquid products were added of a weighed amount of internal standard (*n*-nonane) and analysed by GC. Reported Schulz–Flory α-values were determined from the ratio of C_{10} and C_8 product quantity. The palladium catalysed oligomerisation of propene and 1-butene were conducted in the batch mode in steel autoclaves. In the first case, after filling of the autoclave with the catalyst solution (see above) the desired quantity of propene or 1-butene was pressed under vigorous stirring. After the desired reaction time, the autoclave was cooled in an ice bath and opened. The internal standard was added and the reaction mixture analysed by GC. In order to determine product linearity in high oligomer fraction, a part of the liquid product was hydrogenated on Pd/C and then analysed by CG.

3.8. Typical procedure for ethylene oligomerisation catalysed by [(P^N)$NiBr_2$]/MAO

1.3 ml of a 10% MAO solution in toluene was added to a solution obtained dissolving 0.02 mmol of the relevant (P^N)$NiBr_2$ complex in 19.0 ml toluene (MAO/Ni ≅ 100 mol/mol). The above described procedure was then followed. During the product workup, the excess MAO was quenched with water, and the organic phase extracted with toluene, dried over sodium sulfate and then analysed by GC. In this case, the reported Schulz–Flory α-values were determined from the ratio of C_{12} and C_{10} product quantity. In the case of the obtainment of high molecular weight products, only the TOF was determined.

4. Supplementary material

Supplementary material contains preparation and characterisation of alkylidene anilines ***p-2***, ***p-4***, ***p-5***, ***p-6***, ***p-7***, ***p-8***, as well as of literature known ***p-1*** and ***p-3***. The complete crystallographic data for **2** and **4** are also given. Crystallographic data for these structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 171806 for compound **2**, and 171807 for compound **4**, respectively. Copies of this information may 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).

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