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Preparation and reactions of palladium(0)–olefin complexes with iminophosphine ligands

Simonetta Antonaroli, Bruno Crociani *

Dipartimento di Scienze e Tecnologie Chimiche, Universita' di Roma 'Tor Vergata', Via della Ricerca Scientifica, 00133 Roma, Italy

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Abstract

The complexes [Pd(η^2-*ol*){*o*-(Ph_2P)–C_6H_4–CH=NR}] [*ol*, dimethyl fumarate (*dmf*), 1,4-naphtoquinone (*nq*), fumaronitrile (*fn*); R = C_6H_4OMe-4, CMe_3, Me, bornyl] can be prepared in good yields from the reaction of the allyl derivatives [Pd(η^3-C_3H_5)-{*o*-(Ph_2P)–C_6H_4–CH=NR}]BF_4 with an excess of $NHEt_2$ in the presence of the activated olefin *ol*. The complex [Pd(η^2-*ma*){*o*-(Ph_2P)–C_6H_4-CH=NC_6H_4OMe-4}] (*ma*, maleic anhydride) is more conveniently obtained via olefin substitution from [Pd(η^2-*dmf*){*o*-(Ph_2P)–C_6H_4–CH=NC_6H_4OMe-4}]. The α-diimine ligand of [Pd(η^2-*fn*)(py-2-CH=NC_6H_4OMe-4)] is quantitatively displaced by the appropriate iminophosphine to give [Pd(η^2-*fn*){*o*-(Ph_2P)–C_6H_4–CH=NC_6H_4OMe-4}]. The new zerovalent complexes with P–N ligands are characterized by multinuclear NMR spectroscopy. In solution, olefin rotation or olefin exchange are generally slow. The compound [Pd(η^2-*fn*){*o*-(Ph_2P)–C_6H_4–CH=NC_6H_4OMe-4}] reacts with a second molecule of iminophosphine yielding [Pd(η^2-*fn*){*o*-(Ph_2P)–C_6H_4–CH=NC_6H_4OMe-4}$_2$] in which the iminophosphines act essentially as P-monodentate ligands. [Pd(η^2-*dmf*) {*o*-(Ph_2P)–C_6H_4–CH=NC_6H_4OMe-4}] undergoes fast oxidative addition of allyl chloride to [Pd(η^3-C_3H_5){*o*-(Ph_2P)–C_6H_4–CH=NC_6H_4OMe-4}]$^+$. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Palladium; Alkene complexes; Olefin rotation; Oxidation addition

1. Introduction

The complexes [M(η^2-*ol*)(N–N′)] (M, Pd or Pt; *ol*, olefin; N–N′, bidentate nitrogen-donor ligand of the α-diimine type, such as 1,2-bis(imino)ethanes, 2-(iminomethyl)pyridines, 2,2-bipyridines, 1,10-phenanthrolines, bis(arylimino)acenaphtenes and bis(phenylimino) camphane) are generally prepared from olefinic zerovalent precursors via displacement reactions with the appropriate ligands [1,2]. If this appears to be the best synthetic route for [Pt(η^2-*ol*)(N–N′)] ([1]c), [2], many palladium analogs can be also prepared by reaction (1):

$$[Pd(\eta^3\text{-}2\text{-}RC_3H_4)(N\text{–}N')]^+ + BPh_4^- \xrightarrow[-BPh_3]{+\,ol} [Pd(\eta^2\text{-}ol)(N\text{–}N')] + PhCH_2CR{=}CH_2 \quad (1)$$

(R = H, Me; *ol* = dimethyl fumarate, fumaronitrile, maleic anhydride) which involves a phenyl transfer from BPh_4^- to the allyl group to form allylbenzenes and the palladium(0)-olefin derivative [3]. This is a particular case of the general tendency of cationic allylpalladium(II) complexes to undergo nucleophilic attack by a large variety of nucleophiles, thereby yielding substituted allyl products and palladium(0) species, which may be stabilized by coordination of a π-accepting olefin, as in reaction (1), or may be reoxidized to the starting cationic compounds in the presence of allylic halides or esters, as in the palladium-catalyzed allylic substitutions [4].

In order to extend the synthetic application of nucleophilic attack on allyl palladium(II) substrates, we report herein the preparation of the complexes [Pd(η^2-*ol*)(P–N)] (P–N, bidentate iminophosphine ligand of the *N*-(2-(diphenylphosphino)benzylidene)amine type),

* Corresponding author.

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Table 1
Elemental analysis and selected IR data

Compound			Analysis[a]			IR bands[b]		
			C	H	N	ν(C≡N)	ν(C=O)	ν(C=N)
o-(Ph_2P)–C_6H_4–CH=NR		R						
		C_6H_4OMe-4	79.1 (78.97)	5.7 (5.61)	3.5 (3.54)			1615 ms
		CMe_3	79.7 (79.97)	7.1 (7.00)	3.9 (4.06)			1630 ms
		Me	79.3 (79.19)	6.1 (5.98)	4.5 (4.62)			1638 ms
		bornyl	81.3 (81.85)	7.7 (7.58)	3.3 (3.29)			1630 ms
[Pd(η^2-*ol*){*o*-(Ph_2P)–C_6H_4–CH=NR}]								
	ol	R						
1a	*dmf*	C_6H_4OMe-4	58.9 (59.50)	4.5 (4.68)	2.1 (2.17)		1689 s, 1670 s	1612 m
1b	*fn*	C_6H_4OMe-4	61.8 (62.13)	4.0 (4.17)	7.1 (7.25)	2198 ms		1617 m
1c	*nq*	C_6H_4OMe-4	65.0 (65.51)	4.4 (4.28)	2.1 (2.12)		1630 m, 1590 m	1615 ms
1d	*ma*	C_6H_4OMe-4	59.6 (60.06)	3.9 (4.03)	2.2 (2.33)		1784 s, 1756 m, 1714 s(br)	1608 m
2a	*dmf*	CMe_3	58.7 (58.44)	5.6 (5.41)	2.3 (2.35)		1686 s(br)	1625 m
2b	*fn*	CMe_3	59.9 (61.20)	4.8 (4.95)	7.8 (7.93)	2202 ms, 2192 s		1616 m
3a	*dmf*	Me	56.0 (56.38)	4.8 (4.73)	2.6 (2.53)		1694 s, 1667 s	1634 m
4b	*fn*	bornyl	64.9 (64.97)	5.7 (5.62)	6.6 (6.89)	2203 ms, 2190 s		1607 m

[a] Calculated values in parentheses.
[b] As Nujol nulls.

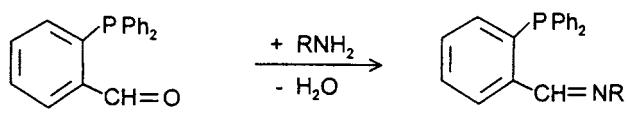
which is essentially based on the amination of the corresponding [Pd(η^3-C_3H_5)(P–N)]$^+$ cations by diethylamine in the presence of activated olefins.

Recently, the palladium(0) derivative [Pd(PNN)], containing the terdentate *N*–(2-(diphenylphosphino) benzylidene)(2-(2-pyridyl)ethyl) amine (PNN) has been synthetized by reacting [Pd(C_3H_5)(PNN)]$^+$ with pyrrolidine [5]. On the other hand, some [Pd(η^2-*ol*)(P–N)] complexes with chiral (aminoferrocenyl)phosphine ligands have been prepared by displacement reactions from [$Pd_2(dba)_3$]·$CHCl_3$ (dba, dibenzylideneacetone) [6].

2. Results and discussion

2.1. Preparation and characterization of the iminophosphine ligands

The *N*-(2-(diphenylphosphino)benzylidene)amines are synthetized in high yield from the condensation reaction of 2-(diphenylphosphino)benzaldehyde [7] with the appropriate primary amine in a CH_2Cl_2/MeOH (1:3 v/v) mixture at r.t.:



(2)

(R = C_6H_4OMe-4, Me, CMe_3, bornyl[1])

Under these conditions, the reaction proceeds smoothly to completion and does not require any heating at higher temperature (e.g. refluxing ethanol [8]), or the presence of a drying agent (e.g. molecular sieves [5,9]), or the use of a large excess of the amine (e.g. neat *tert*-butylamine [10]).

The iminophosphines are characterized by elemental analysis, IR spectra (Table 1) and by multinuclear NMR spectra (Tables 2 and 3). The NMR spectra of *o*-(Ph_2P)–C_6H_4CH=NR (R = bornyl) indicate the presence of a minor isomer in solution (ca. 9%), which may be due either to an *exo* structure of the *N*-substituent or to a *Z* configuration of the aldimine group in

[1] bornyl, *endo*-(IR)-1,7,7-trimethylbicyclo [2.21]hept-2-yl.

Table 2
Selected ^{1}H- and ^{31}P-{^{1}H}-NMR data[a]

Compound			Iminophosphine protons				Olefin protons			^{31}P resonances
			N=C*H*	N–C*H*	C(CH_3)$_3$	OCH_3	=C*H*	OCH_3		
o-(Ph_2P)–C_6H_4–CH=NR										
		R								
		C_6H_4OMe-4	9.06 d (4.4)[b]			3.78 s				−15.56 s
		CMe_3	8.77 d (4.2)[b]		1.04 s					−14.50 s
		Me	8.92 d (3.7)[b]	3.37 s						−16.83 s
		bornyl	8.73 d (5.3)[b]	3.29 m						−14.97 s
			8.71[c]	3.06[c] m						−16.68[c] s
[Pd (η^2-*ol*){*o*-(Ph_2P)–C_6H_4–CH=NR}]										
	ol	R								
1a	*dmf*	C_6H_4OMe-4	8.11 d (4.0)			3.81 s	4.23 d, (9.9)[e]	3.22[d] dd (9.9)[b]	3.32 s, 3.14 s	19.24 s
1b	*fn*	C_6H_4OMe-4	8.18 d (3.2)[b]			3.81 s	3.22 dd, (9.8)[e] (3.3)[b]	2.46[d] dd (9.8)[b]		18.24 s
1c	*nq*	C_6H_4OMe-4	8.05 d (4.3)[b]			3.86 s	4.83 d, (4.5)[e]	4.48[d] dd (10.0)[b]		24.12 s
1d	*ma*	C_6H_4OMe-4	8.11 d (3.9)[b]			3.83 s	4.24 dd, (4.1)[e] (3.2)[b]	3.61[d] dd (10.4)[b]		21.57 s
2a	*dmf*	CMe_3	8.08 d (3.5)[b]		1.28 s		4.12 d, (10.2)[e]	3.69[d] dd (10.2)[b]	3.54 s, 3.14 s	22.61 s
2b	*fn*	CMe_3	8.11 s		1.28 s		3.13 d, (10.0)[e]	2.65[d] dd (10.0)[b]		20.71 s
3a	*dmf*	Me	8.15 s	3.93 s			4.22, d (10.1)[e]	3.89[d] dd (10.1)[b]	3.66 s, 3.15 s	17.99 s
4b	*fn*	bornyl	8.21 d (2.7)[b]	3.60 m			3.12 d, (9.6)[e] (3.4)[b]	2.77[d] dd (9.6)[b]		19.41 s
			8.29[f] d (2.2)[b]	4.42[f] m			mk, 9.6)[b] (9.6)[e]	2.58[d,f] dd		

[a] In $CDCl_3$ at 30°C; satisfactory integration values were obtained; coupling constants in Hz; mk, masked; s, singlet; d, doublet; dd, doublet of doublets; m, multiplet.
[b] *J*(PH).
[c] Minor isomer (see text).
[d] *Trans* to phosporus.
[e] *J*(HH).
[f] Minor diasteroisomer (see text).

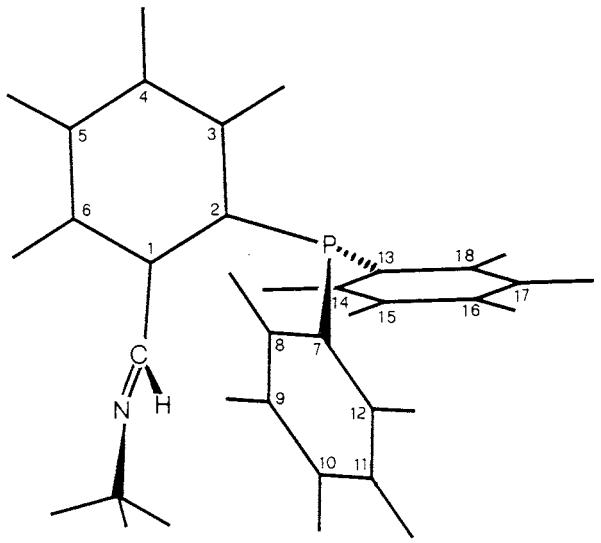
equilibrium with the more stable *E* isomer [11]. Inspection of the ^{1}H-NMR spectrum of the commercial (*R*)-(+)-bornylamine, used in the synthesis of the ligand, shows that the *endo*-(1*R*) form is predominant in $CDCl_3$ solution (ca. 97%). On the other hand, no isomeric species attributable to an *exo* structure of the *N*-bornyl fragment is observed in the ^{1}H- and ^{31}P-NMR spectra of the complex [$PtCl_2${*o*-(Ph_2P)–C_6H_4–CH=NR}] (R = bornyl) in which the aldimine function is forced by chelation to assume exclusively the *E* configuration. These pieces of evidence therefore suggest the *E*–*Z* isomerism to be the more likely explanation for the solution behaviour of the uncoordinated iminophosphine ligand. The larger size of the bornyl group, compounded with the bulkiness of the *o*-Ph_2P substituent, seems to play an important role in stabilizing the *Z* isomer in line with the steric effects observed for *ortho*-substituted aryl aldimines [11].

The 2D ^{1}H-NMR spectrum of *o*-(Ph_2P)–C_6H_4–CH=NMe in $CDCl_3$ shows an intense NOE between the imino proton and the NMe protons, in accordance with an *E* configuration of the imino function, and two

Table 3
Selected ^{13}C-{^{1}H}-NMR data[a]

Compound			Iminophosphine carbons				Olefin carbons			
			N=*C*H	N–*C*	C(*C*H$_3$)$_3$	O*C*H$_3$	=*C*–H	*C*≡N	O*C*H$_3$	*C*=O
o-(Ph$_2$P)–C$_6$H$_4$–CH=NR										
		R								
		C$_6$H$_4$OMe-4	156.68 d (21.4)	144.54		55.34				
		CMe$_3$	154.37 d (20.3)	57.67	29.43					
		Me	160.88 d (24.0)	47.90						
		bornyl	157.80 d (18.9)	75.75						
			156.06[b] d (24.4)	78. 88[b]						
[Pd (η^2-*ol*){*o*-(Ph$_2$P)–C$_6$H$_4$–CH=NR}]										
	ol	R								
1a	*dmf*	C$_6$H$_4$OMe-4	164.62	148.66		55.48	50.4 ÷ 50.0[c]		50.4 ÷ 50.0[c]	173.83, 173.56
1b	*fn*	C$_6$H$_4$OMe-4	165.26	148.34		55.48	25.32, 24.26[d] d (44.8)	123.13 d (8.4)		
1c	*nq*	C$_6$H$_4$OMe-4	164.97	146.87		55.46	63.79, 66.27[d] d (20.4)			183.91, 182.83
1d	*ma*	C$_6$H$_4$OMe-4	165.26	147.81		55.46	47.93, 49.24[d] d (32.4)			172.47, 171.33
2a	*dmf*	CMe$_3$	160.61	62.86	29.44		47.63, 48.37[d] d (32.4)		50.23	173.91
2b	*fn*	CMe$_3$	161.39	63.50	29.48		22.82, 22.81[d] d (46.2)	122.54, 123.92 d (8.4)		
3a	*dmf*	Me	165.10	57.12			48.99, 48.60[d] d (30.3)		50.45, 50.15	173.92
4b	*fn*	bornyl	166.25	82.60			23.21, 23.84[d] d (46.2)	123.64, 122.02		
			163.79[e]	81.29[e]						

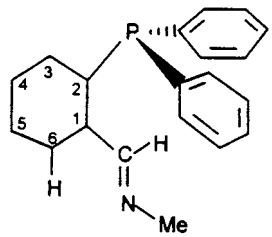
[a] In $CDCl_3$ at 30°C; *J*(PC) coupling constants (Hz) in parentheses.
[b] Minor isomer (see text).
[c] Overlapping signals.
[d] *Trans* to phosphorus.
[e] Minor diasteroisomer (see text).



Imino proton distances (Å)	Torsion angles (°)
N=C-H · · ·H(6) = 3.35	H-C-C(1)-C(6) = 114
N=C-H · · ·H(8) = 2.84	C(1)-C(2)-P-C(7) = 35
N=C-H · · ·H(12) = 4.02	C(8)-C(7)-P-C(2) = 56
N=C-H · · ·H(14) = 3.73	C(14)-C(13)-P-C(2) = 17
N=C-H · · ·H(18) = 5.76	
N=C-H · · ·H(9) = 3.71	

Fig. 1. Perspective view of the most stable conformation for *o*-(Ph_2P)–C_6H_4–CH=NMe, with phenyl carbon numbering scheme and some selected atomic distances and torsion angles.

weaker NOEs of the imino proton with the H(6) proton of the 1,2-disubstituted phenyl group and with the *ortho* protons of the Ph_2P phenyl groups. These findings may be interpreted in terms of a predominant conformation of type **I**:



where the imino group lies on the side opposite to the phosphorus lone pair (relative to the P–C(2) bond) and the imino C–H bond is on the side opposite to the C(6)–H(6) bond. In this conformation, the imino proton may be at relatively short distance from the Ph_2P *ortho* protons, comparable with that from the H(6) proton.

Interestingly, model calculations have shown that conformations similar to **I** are predominant also for the isolated molecule. The most stable of these conformations is reported in Fig. 1, along with some selected atomic distances and torsion angles.

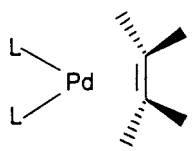
2.2. Preparation and characterization of the complexes [Pd(η^2-ol)(P–N)]

These complexes are prepared by reactions (3–6) of Scheme 1.

In contrast to the corresponding reaction with [Pd(η^3-C_3H_5)(N–N′)]ClO_4 (N–N′ = α-diimine) [3], the phenylation of the allyl complexes [Pd(η^3-C_3H_5)(P–N)]BF_4 by $NaBPh_4$ in the presence of activated olefins [Eq. 3] requires heating at 60–70°C to proceed at reasonable rate. At that temperature, however, partial decomposition of the products to metallic palladium reduces considerably the yield in [Pd(η^2-*ol*)(P–N)]. The latter compounds are more conveniently obtained from amination of [Pd(η^3-C_3H_5)(P–N)]BF_4 by diethylamine according to reaction (4), which occurs rapidly at ambient temperature when a moderate excess of the amine is used. This method, however, cannot be applied for the preparation of palladium(0) derivatives with η^2-bound maleic anhydride due to the reactivity of this ligand towards $NHEt_2$. The *ma* complex **1d** is therefore synthetized from the substitution reaction (5) involving the preformed *dmf* derivative **1a**. On the other hand, reaction (6) provides another synthetic route through displacement of α-diimine ligands from zerovalent palladium complexes by iminophosphines. As indicated by ^{1}H-NMR spectra, the 2-(iminomethyl)pyridine ligand of [Pd(η^2-*fn*)(py-2-CH=NC_6H_4OMe-4)] [3] is rapidly and quantitatively displaced by *o*-(Ph_2P)–C_6H_4–CH=NC_6H_4OMe-4 when the reactants are mixed in a 1:1 molar ratio in $CDCl_3$ solution.

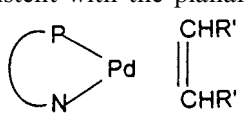
The elemental analyses and some selected IR, ^{1}H-, ^{31}P- and ^{13}C-NMR data of complexes **1a**–**4b** are listed in the Tables 1–3.

According to X-ray structural data, the complexes [Pd(η^2-*ol*)L_2] have a trigonal planar coordination around the palladium center as in structure **II**:

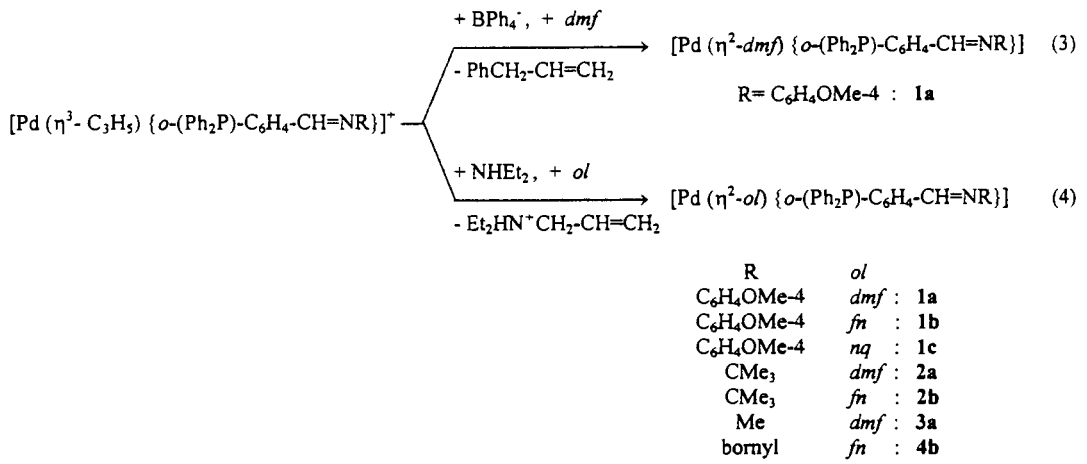


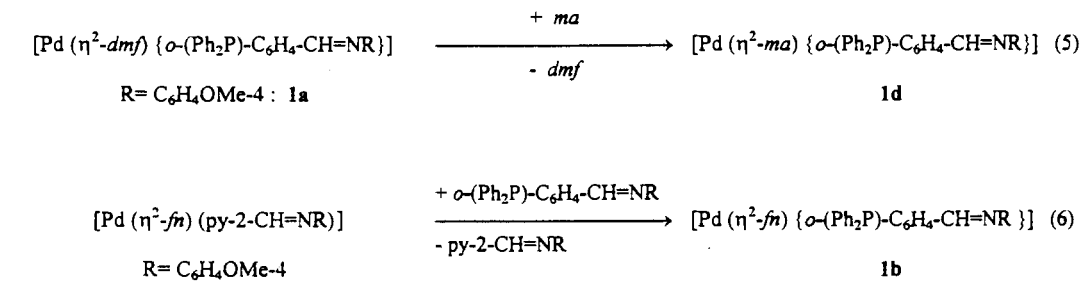
II

in which the plane passing through palladium and the olefinic carbons is almost coplanar with the PdL_2 plane ([1]c) [6,12]. In view of the chelating properties of the iminophosphine ligands [5] ([8]b,c) [10], a structure of type **II** is assumed to be extant also for the [Pd(η^2-*ol*)(P–N)] compounds. The ^{1}H- and ^{13}C-NMR spectra are in fact consistent with the planar geometry **III**:



III





[*ol*= dimethyl fumarate (*dmf*), fumaronitrile (*fn*), 1,4- naphtoquinone (*nq*), maleic anhydride (*ma*)]

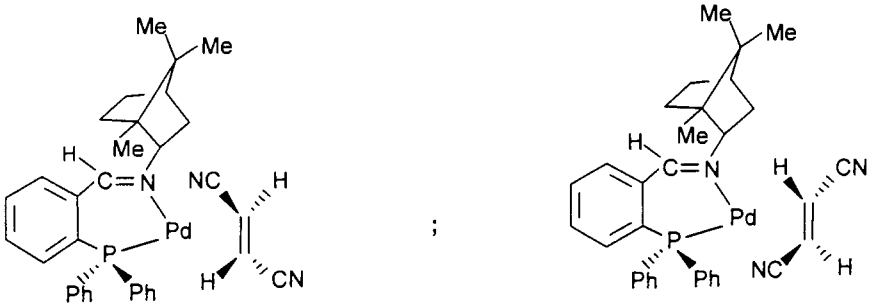
Scheme 1.

as suggested by the larger J(PC) and J(PH) coupling constants of the olefinic =CH fragment *trans* to phosphorus relative to those of the *cis* = CH moiety. In the complexes **1a–4b** the ^{31}P signals of the PPh_2 group and the ^{1}H and ^{13}C signals of the imino group –CH=NR are generally shifted downfield if compared to the corresponding signals of the uncoordinated iminophines, indicating that σ donation predominates in the P–N bonding. A noticeable exception is given by the imino proton resonance which undergoes an upfield shift of 0.6–1.0 ppm, probably due to a conformational change of the ligand upon chelation.

For the η^2–bound olefins, upfield shifts of 2.5–3.8 ppm for the alkenic protons, and of 75–97 ppm for the alkenic carbons are observed in the ^{1}H- and ^{13}C-NMR spectra, respectively, in comparison to the corresponding signals of the free ligands, which occur at 6.86 (^{1}H) and 133.9 (^{13}C) ppm for *dmf*, at 6.99 and 138.6 ppm for *nq*, at 6.29 and 119.8 ppm for *fn*, and at 7.04 and 137.1 ppm for *ma*, in $CDCl_3$. These changes clearly arise from extensive electron donation from the d^{10} palladium center to the olefin, which is also reflected by the low-frequency shifts of the alkenic ν(C=O) and ν(C≡N) bands in the IR spectra of **1a–4b** [cf. the ν(C=O) bands at 1725 cm^{-1} for *dmf*, at 1650 cm^{-1} for *nq*, at 1850, 1792 and 1780 cm^{-1} for *ma*, and the ν(C≡N) band at 2244 cm^{-1} for *fn*]. In contrast, the ν(C=N) absorptions of the imino group are scarcely affected by coordination, in line with the observation that the C=N bond distances of α-diimines undergo only a slight lengthening in the coordination to palladium(II) and palladium(0) centers ([1]c) [13]. Thus, π back-donation from the electron rich metal center to the activated alkene appears to be the predominating factor in stabilizing the zerovalent complexes [Pd(η^2-*ol*)(P–N)], as was earlier reported for [Pd(η^2-*ol*)(N–N′)] (N–N′ = α-diimine) [1b–1d, 3]. Accordingly, the electron accepting abilities of the olefin are important for the preparation of stable complexes: attempts to isolate complexes of type [Pd(η^2-*ol*)(P–N)] with less π-accepting olefins, such as methyl acrylate or acrylonitrile, were unsuccessful.

In contrast to the solution behaviour of [Pd(η^2-*ol*)(N–N′)] (N–N′ = α-diimine) ([1]c) [3], for the [Pd(η^2-*ol*)(P–N)] analogs the dynamic processes, such as olefin rotation or olefin dissociation-association, are slow, if they occur, on the NMR time scale at 30°C in $CDCl_3$. In the ^{1}H and ^{13}C-NMR spectra, the non-equivalent hydrogens and carbons of the η^2-bound

CH=CH olefinic unit appear as two distinct and sharp signals. The low rate (or absence) of olefin dissociation can be also inferred by the detection of two diastereoisomers for complex **4b**, containing the chiral *o*-(Ph_2P)–C_6H_4–CH=NR (R = bornyl) ligand, in the ratio of ca. 1:7.8:



Owing to the *trans* geometry of fumaronitrile, interconversion of these isomers can occur only through olefin (or P–N ligand) dissociation-association equilibria.

The lack of dissociation–association equilibria of this type has been also reported for the related complexes [Pd(η^2-*ol*)(P–N)] with *ol* = *ma*, *dmf* and P–N = chiral (aminoferrocenyl)phosphine [6]. For the latter compounds, however, rotation of the coordinated olefin was observed with coalescence of the alkenic ^{1}H resonances generally occurring at rather high temperatures (313–373 K). In our case, the study of the fluxional behaviour at higher temperatures was hampered by partial decomposition of the complexes to palladium metal (which was particularly extensive for the *dmf* derivatives).

2.3. Reactions of the complexes [Pd(η^2-ol)(P–N)]

2.3.1. Ligand exchange and substitution

The reactions involving olefin exchange or substitution occur according to the equilibrium (7):

$$[Pd(\eta^2\text{-}ol)(P\text{–}N)] + ol' \leftrightarrows [Pd(\eta^2\text{-}ol')(P\text{–}N)] + ol \qquad (7)$$

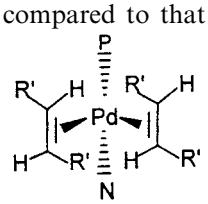
where the entering olefin *ol′* may be identical to or different from the coordinated olefin *ol* in the starting compound.

As indicated by ^{1}H-NMR spectra in $CDCl_3$, the η^2-bound *dmf* ligand of **1a** is readily and quantitatively substituted by 1 equivalent of any of the other olefins. As mentioned before, such a reaction has been used for the preparation of the *ma* derivative **1d** [Eq. (5) of Scheme 1]. Similarly, a quantitative substitution of the η^2-bound *nq* ligand takes place in the reactions of **1c** with 1 equivalent of *fn* or *ma*.

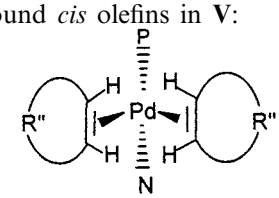
Both reactions of the fumaronitrile complex **1b** with *ma* (1:1 molar ratio) and of the maleic anhydride complex **1d** with *fn* (1:1 molar ratio) lead to the same equilibrium mixture in $CDCl_3$, in which a **1b**:**1d** ratio of 1:1.6 is observed. These results closely parallel those reported for analogous olefin substitutions on [Pd(η^2-*ol*)(N–N′)] (N–N′ = bis(arylimino)acenapthenes or bis(phenylimino)camphane ([1]c) and 2-(iminomethyl) pyridines ([1]d)), and provide further evidence to the increasing stabilization of the zerovalent palladium–olefin compounds with increasing electron accepting abilities of the olefinic ligands.

In the presence of free olefin, the α-diimine complexes [Pd(η^2-*ol*)(N–N′)] undergo fast exchange (on the NMR time scale) between free and coordinated olefin, the rate of which decreases with decreasing concentration of the reactants and with increasing steric demand of both the α-diimine and olefinic ligands, in agreement with an essentially associative mechanism analogous to that proposed for olefin substitutions ([1]c), ([1]d).

For equimolar [Pd(η^2-*ol*){*o*-(Ph_2P)–C_6H_4–CH=NC_6H_4OMe-4}]/*ol* solutions in $CDCl_3$, such exchange was found to occur at considerably reduced rates, even at 30°C and with complex and olefin concentrations as high as 2.5×10^{-2} mol dm^{-3}. In the ^{1}H-NMR spectra, the exchange brings about only some broadening of the signals for the free and coordinated olefin, without any coalescence or significant change in chemical shifts, relative to those of $CDCl_3$ solutions containing the olefin or the complex alone. The broadening is more pronounced for *cis* olefins, *nq* and *ma*, than for *trans* olefin, *dmf* and *fn*, suggesting a slightly higher exchange rate for the former ligands. In terms of the proposed associative mechanism through a labile 18-electron intermediate [Pd(η^2-*ol*)$_2$(P–N)], these findings may be rationalized if one considers the greater steric demand of the iminophosphine *o*-(Ph_2P)–C_6H_4–CH=NC_6H_4OMe-4 compared to that of an α-diimine such as py-2-CH=NC_6H_4OMe-4, and the greater steric interaction between the η^2-bound *trans* olefins in the intermediate **IV** compared to that of the η^2-bound *cis* olefins in **V**:



IV



V

The reactions involving exchange of the iminophosphine ligands occur according to equilibrium (8):

$$[Pd(\eta^2\text{-}ol)(P-N)] + P-N \leftrightarrows [Pd(\eta^2\text{-}ol)(P-N)_2] \quad (8)$$

These reactions have been studied for the fumaronitrile complexes **1b** and **2b** in the presence of 1 equivalent of the corresponding P–N ligand. The exchange rate and the equilibrium position depend markedly on the nitrogen substituent. The ^{1}H-NMR spectra of an equimolar **1b**/*o*-(Ph_2P)–C_6H_4–CH=NC_6H_4OMe-4 solution in $CDCl_3$ show a fast exchange (on the NMR time scale) with the equilibrium being almost completely shifted to the right. At 30°C, time-avered signals are detected for both the iminophosphine (e.g. a single broad resonance for the imino protons at 8.73 ppm) and the olefin (a single broad resonance for the olefinic protons at 2.70 ppm). At −40°C (the lowest temperature explored), the signals sharpen but no appreciable amount of the reactants **1b** and free iminophosphine is observed. For this reason, the product [Pd(η^2-*fn*) {*o*-(Ph_2P)–C_6H_4–CH=NC_6H_4OMe-4}$_2$] can be isolated and characterized (see Section 3). The multinuclear NMR spectra of this compound suggest that the olefin is η^2-bound to the metal [δ(=C*H*) as a broad singlet at 2.70 ppm, and δ(=*C*H) as a broad singlet at 36.5 ppm], while the iminophosphines very likely act as P-monodentate ligands [δ(^{31}P) as a singlet at 17.5 ppm; δ(N=C*H*) as a broad singlet at 8.73 ppm, δ(N=*C*H) and δ(N–*C*) as broad singlets at 156.0 and 144.5 ppm, respectively]. If compared with the imino function resonances of the free *o*-(Ph_2P)–C_6H_4–CH=NC_6H_4OMe-4 [Tables 2 and 3], the imino proton signal in the complex appears to be shifted upfield of 0.33 ppm, while the carbon signals are nearly coincident.

The ^{1}H-NMR spectra of an equimolar **2b**/*o*-(Ph_2P)–C_6H_4–CH=$NCMe_3$ solution in $CDCl_3$ at 30°C show that the exchange rate is slow and, when the equilibrium is reached, the mixture consists of a 1:1:9.5 molar ratio of **2b**, P–N and [Pd(η^2-*fn*) (P–N)$_2$], respectively. The latter complex was not isolated, but was identified from its ^{1}H-NMR spectrum, characterized by the signals of the imino proton (a sharp singlet at 8.65 ppm), of the η^2-bound olefin (a sharp doublet at 2.66 ppm with *J*(PH) of 3.7 Hz) and of the CMe_3 group (a sharp singlet at 0.93 ppm). The corresponding integration values are in agreement with the proposed formulation. Also for [Pd(η^2-*fn*){*o*-(Ph_2P)–C_6H_4–CH=$NCMe_3$}$_2$] the ^{1}H imino function resonances are close to those of the free iminophosphine (Table 2), suggesting a P-monodentate coordination for this ligand.

A P-monodentate coordination of the rigid ligand 1-(dimethylamino)-8-(diphenylphosphino)naphtalene (PAN) in *trans*-[$PdCl_2$(PAN)$_2$] was demonstrated by an X-ray structural determination [14].

2.3.2. Oxidative addition of allyl chloride

The *dmf* complex **1a** undergoes a fast oxidative addition of allyl chloride at ambient temperature, yielding the cationic complex [Pd(η^3-C_3H_5){*o*-(Ph_2P)-C_6H_4–CH=NC_6H_4OMe-4}]$^+$ which was isolated as BF_4^- salt and identified by comparing its ^{1}H-NMR with that of an authentic sample independently prepared.

3. Experimental

The ^{1}H-, ^{13}C-{^{1}H}- and ^{31}P-{^{1}H}-NMR spectra were recorded on a Bruker AM400 spectrometer, operating at 400.13, 100.61 and 161.98 MHz, respectively. Chemical shifts (ppm) are given relative to TMS (^{1}H-, ^{13}C-NMR) and 85% H_3PO_4 (^{31}P-NMR). The ^{1}H 2D ROESY spectrum of *o*-(Ph_2P)–C_6H_4–CH=NMe in $CDCl_3$ was obtained in the phase-sensitive mode using the TPPI phase cycle with the ROESY pulse sequence, modified to eliminate the offset dependence of cross-peak intensity [15]. A total of 128 transients on a size of 2K were accumulated for 512 experiments. A spinlock period corresponding to a transverse mixing time of 0.3 s was applied. Data were processed with the 2-D NMR program TRITON, licensed by the University of Utrecht, The Netherlands. A sine bell apodization function, shifted by $\pi/3$, was applied in both dimension as to obtain a 1K × 1K real matrix. We thank Fabio Bertocchi for technical support in running the NMR spectra.

The IR spectra of solid samples were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer 983 G instrument using CsI windows.

Model calculations were performed with version 5.0 of the HyperChem package (Hypercube, Waterloo, Ontario) running on a Pentium Pro-133 MHz microprocessor. The geometry of the model compound *o*-(Ph_2P)–C_6H_4–CH=NMe, with an *E* configuration for the imine function, was optimized by the AM1 method [16] implemented in HyperChem, up to a RMS gradient $\leq$ 0.01 kcal Å^{-1} mol^{-1} (heat of formation = 123.93 kcal mol^{-1}). The conformational search for finding low energy conformations of the molecule was carried out by varying of 30° the dihedral angles concerning the rotation of the phenyl planes around the phosphorus–phenyl bonds, and the rotation of the imino group plane (–CH=N–Me) around its bond to the C_6H_4 fragment. We thank M.L. Di Vona of Dipartimento di Scienze e Tecnologie Chimiche, Universita' di Roma 'Tor Vergata', for running the model calculations.

The complexes [$PtCl_2$(COD)] (COD = 1,5-cyclooctadiene) [17] [Pd(μ-Cl) (η^3-C_3H_5)]$_2$ [18] and [Pd(η^2-*fn*)(py-2-CH=NC_6H_4OMe-4)] [3] were prepared by literature methods. The commercial *p*-anisidine was sublimed at low pressure before use. All other chemicals and solvents were reagent grade, and were used without further purification.

3.1. Preparation of the iminophosphines *o*-(Ph_2P)–C_6H_4–CH=NR

The 2-(diphenylphosphino)benzaldehyde [7] (1.16 g, 4 mmol) and the required amount of the appropriate amine RNH_2 were dissolved in 200 cm^3 of a MeOH/CH_2Cl_2 mixture (3:1 v/v) under N_2. For R = C_6H_4OMe-4 and Me, an aldehyde/amine molar ratio of 1:1.1 was used, whereas for the more sterically demanding bornyl and CMe_3 substituents the ratio was increased to 1:1.5 and 1:3, respectively. In the case of $MeNH_2$, 0.38 cm^3 of a 40% acqueous solution of the amine was used. The progress of the reaction was monitored by IR spectroscopy, following the decay of the aldehyde ν(C=O) band at 1695 cm^{-1}. The completion was reached in ca. 2 h for R = Me, 3–4 h for R = C_6H_4OMe-4 and bornyl, and 7 h for R = CMe_3. After standing overnight at r.t., the solution was concentrated to small volume (ca. 5 cm^3) and kept at −20°C for 24 h. The microcrystalline solids were filtered off and washed with cold methanol. For the more soluble iminophosphines (R = bornyl and CMe_3), the mother liquor resulting from filtration and MeOH washing was concentrated and cooled at −20°C to give a second crop of solid product. The yields were in the range 76–92%.

3.2. Preparation of [$PtCl_2${*o*-(Ph_2P)–C_6H_4–CH=NR}] (R = bornyl)

A solution of the P–N ligand (0.14 g, 0.33 mmol) in 5 cm^3 of benzene was added to a solution of [$PtCl_2$(COD)] (0.10 g, 0.27 mmol) in 5 cm^3 of CH_2Cl_2. After stirring for 2 h, the product separated as a white solid. The precipitation was completed by dilution with diethyl ether (0.16 g, 85.7 %). The complex was characterized by elemental analysis (Found: C, 50.7; H, 4.7; N, 2.0. $C_{29}H_{32}Cl_2NPPt$ calcd.: C, 50.37; H, 4.66; N, 2.03%), IR spectrum as Nujol mull [ν(C=N) at 1620 cm^{-1}; ν(Pt–Cl) at 342 and 279 cm^{-1}], ^{1}H- and ^{31}P-NMR spectra in $CDCl_3$ [δ(N=C*H*) at 8.36 ppm with J(PtH) = 109 Hz; δ(^{31}P) at 2.05 ppm with J(PtP) = 3828 Hz].

3.3. Preparation of [Pd(η^3-C_3H_5)(P–N)]BF_4

These complexes were prepared from the reaction of [Pd(μ-Cl)(η^3-C_3H_5)]$_2$ (0.5 mmol) with the appropriate iminophosphine P–N (1 mmol) in the presence of an excess of $NaBF_4$ (2 mmol), in the same way as described for [Pd(η^3-2-MeC_3H_4)(py-2-CH=NC_6H_4OMe-4)]BF_4 [19]. The products were isolated in high yields (88–95%) and characterized by electric conductivity measurements, elemental analysis, IR and multinuclear NMR spectra. As an example, for [Pd(η^3-C_3H_5){*o*-(Ph_2P)–C_6H_4–CH=NC_6H_4OMe-4}]BF_4 the following data were obtained: molar conductivity, 96.5 ohm^{-1} cm^2 mol^{-1} for a 10^{-3} mol dm^{-3} MeOH solution at 25°C; analysis (Found: C, 55.2; H, 4.3; N, 2.1. $C_{29}H_{27}BF_4NOPPd$ calcd.: C, 55.31; H, 4.32; N, 2.22%); IR spectrum as Nujol mull [ν(C=N) at 1612 cm^{-1}, ν(B–F) at 1060 cm^{-1}]; ^{1}H- and ^{31}P-NMR spectra in $CDCl_3$ [P–N protons, δ 8.33 (d, J(PH) = 2.8 Hz, N = C*H*), 3.81 (s, OCH_3); allyl protons, *trans* to phosphorus: δ 4.06 (dd, J(HH) = J(PH) = 6.7 Hz, H_{syn}), 3.65 (dd, J(HH) = 14.2 and J(PH) = 9.5 Hz, H_{anti}), *trans* to nitrogen: δ 3.45 (d(br), J(HH) = 5.0, H_{syn}), 2.96 (d(br), J(HH) = 12.1, H_{anti}); d(^{31}P), 22.07(s)].

3.4. Preparation of [Pd(η^2-ol)(P–N)] (**1a**–**4b**)

3.4.1. Allylic amination

A moderate excess of $NHEt_2$ (2.5 mmol) was added to a solution of [Pd(η^3-C_3H_5)(P–N)]BF_4 (0.5 mmol) and the olefinic ligand *ol* (0.6 mmol) in CH_2Cl_2 (20 cm^3). After standing for 2 h at r.t., the solvent was evaporated to dryness. The solid residue was repeatedly washed with water, dried under vacuum and redissolved in CH_2Cl_2 (20 cm^3). Upon treatment with activated charcoal and filtration, the resulting solution was washed with ca. 50 cm^3 of a 0.1 mol dm^{-3} aqueous solution of Na_2CO_3 and then with ca. 50 cm^3 of water to remove the residual traces of ammonium salts. After drying over Na_2SO_4, the CH_2Cl_2 solution was concentrated to small volume and diluted with *n*-hexane/diethyl ether (1:1 v/v) to precipitate the palladium(0) products, which were recrystallized from the same solvent mixture (yields in the range 78–90%).

3.4.2. Ligand substitution

1. Maleic anhydride (0.06 g, 0.6 mmol) was added to a solution of **1a** (0.26 g, 0.4 mmol) in $CHCl_3$ (20 cm^3). After 0.5 h, the solution was concentrated to small volume and diluted with diethyl ether to precipitate the product [Pd(η^2-*ma*){*o*-(Ph_2P)–C_6H_4–CH=NC_6-H_4OMe-4}] (**1d**), which was recrystallized from the same solvent mixture (0.20 g, 83.3 %).
2. The ligand *o*-(Ph_2P)–C_6H_4–CH=NC_6H_4OMe-4 (0.40 g, 1.01 mmol) was added to a solution of [Pd(η^2-*fn*)(py-2-CH=NC_6H_4OMe-4)] (0.40 g, 1.01 mmol) in $CHCl_3$ (80 cm^3). After 1h, the solution was concentrated to small volume and diluted with diethyl ether to precipitate the product **1b** (0.54 g, 92.2 %).

3.5. Preparation of [Pd(η^2-*fn*){*o*-(Ph_2P)–C_6H_4–CH=NC_6H_4OMe-4)}$_2$]

A solution of the ligand *o*-(Ph_2P)–C_6H_4–CH=NC_6H_4OMe-4 (0.059 g, 0.15 mmol) and of **1b** (0.087 g, 0.15 mmol) in CH_2Cl_2 (30 cm^3) was stirred for

0.5 h at r.t.. Upon concentration and dilution with diethyl ether, the product precipitated as a yellow powder (0.123 g, 84%). This complex was characterized by elemental analysis (Found: C, 69.2; H, 4.6; N, 5.7; $C_{56}H_{46}N_4O_2P_2Pd$ calcd.: C, 68,96; H, 4.75; N, 5.74), IR spectrum as Nujol mull [ν(C≡N) at 2203 cm^{-1}; ν(C=N) at 1627 and 1613 cm^{-1}], and by ^1H-, ^{13}C- and ^{31}P-NMR spectra in $CDCl_3$ (see text).

3.6. Oxidative addition of allyl chloride to **1a**

Allyl chloride (0.04 cm^3, 0.5 mmol) was added to a solution of **1a** (0.16 g, 0.25 mmol) in CH_2Cl_2 (10 cm^3) under N_2. The colour changed immediately from deep-red to yellow–orange. The IR spectrum showed the complete disappearance of **1a** and the presence of uncoordinated *dmf* [ν(C=O) at 1725 cm^{-1}]. After stirring for 0.5 h, a solution of $NaBF_4$ (0.06 g) in MeOH (5 cm^3) was added, and the mixture was worked up as for the preparation of [Pd(η^3-C_3H_5)(P–N)]BF_4, to give [Pd(η^3-C_3H_5){*o*-(Ph_2P)–C_6H_4–CH=NC_6H_4OMe-4}]BF_4 (0.13 g, 82.6 %).

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