ELSEVIER

Journal of Organometallic Chemistry 488 (1995) 223–232

Journal of Organometallic Chemistry

The reactions of tridentate cationic palladium(II) complexes with olefins and nucleophiles [☆]

Heinz-Bernhard Kraatz, David Milstein *

Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot 76100, Israel

Received 19 September 1994

Abstract

The reaction of the chelating bisphosphine 1,3-bis(diphenylphosphino)xylene (dppxH) **1** with $PdCl_2(NCMe)_2$ gives (dppx)PdCl **3**. Analogously, 1,3-bis(bis(*p*-dimethylaniline)phosphino)xylene (dappxH) **2** yields (dappx)PdCl **4**. Halide abstraction with $AgBF_4$ leads cleanly to the ionic complexes $[(dppx)Pd\text{-}solv]^+(BF_4)^-$ **5** and $[(dappx)Pd\text{-}solv]^+(BF_4)^-$ **6** (solv = solvent); in solution, there is no evidence for interaction between anion and cation. Norbornene adds to **5** and **6** to give the corresponding olefin complexes $[(dppx)Pd(nor)]^+(BF_4)^-$ **7** $[(dappx)Pd(nor)]^+(BF_4)^-$ **8**. The olefin is only weakly bound to the metal center and can be easily displaced by nucleophiles, as demonstrated by the reaction of **7** with HO^-, MeO^-, $CH_2{=}CH(CH_2)_4O^-$ and NH_2Ph, to give the corresponding Pd(II)–Nuc complexes, (dppx)PdOH **10**, (dppx)PdOMe **11**, $(dppx)PdO(CH_2)_4CH{=}CH_2$ **12** and $[(dppx)PdNH_2Ph]^+(BF_4)^-$ **13**. The crystal structure of $[(dppx)PdNH_2Ph]^+(BF_4)\cdot 1.5\ CH_2Cl_2$ **13** has been determined by an X-ray diffraction study at 113 K. The angle P(1)–Pd–P(2) is 160.8(3)°, indicating substantial steric congestion because of the size of the aniline ligand. In the solid state, cation and anion are associated via hydrogen bonding in a N–H · · · F bridge.

Keywords: Palladium; Olefin complexes; Crystal structure; Nucleophile; Alkoxidc; Biphosphine

1. Introduction

Palladium–olefin complexes are known to be key intermediates in a series of synthetically important processes [1]. Such a process is the industrial Wacker oxidation, in which ethylene is oxidized to acetaldehyde in aqueous medium. Variations of this method involving use of other olefins can be used to produce acetals, ketals, enol ethers, and esters. Although several mechanistic [2,3] and theoretical [4] studies have been reported over the years, it is still a matter of controversy whether the attack on the coordinated olefin by hydroxide ion occurs in the outer sphere, or whether an internal-sphere process takes place (e.g. olefin insertion into the Pd–O bond or OH migration). The nucleophilic *trans* addition of water or hydroxide to a Pd(II)-coordinated mono-olefin to form a β-hydroxyalkyl palladium(II) species is thought to be one of the key steps in the Wacker oxidation of ethene to acetaldehyde [2].

Although a simple β-hydroxyalkyl palladium(II) intermediate has never been directly observed, such species are stable in the case of chelated diolefins. For example, $[(1,5\text{-COD})PdCl]_2$ undergoes a facile nucleophilic attack under basic conditions to give the corresponding σ-bonded hydroxy-enyl complex [3].

In this paper we discuss the stabilities of tridentate Pd(II)–olefin complexes and their reactions with anionic oxygen-based nucleophiles, such as ^-OH, ^-OMe, and $^-O(CH_2)_4CH{=}CH_2$, and with neutral nucleophiles, such as aniline and THF.

We chose simple Pd(II) complexes with a rigid tridentate bisphosphine ligand framework for our studies. Ligand dissociation is unlikely, and hence β-H elimination from the proposed β-hydroxy intermediate to form the aldehyde is not expected. Furthermore, this ligand

---

[☆] Dedicated to Professor Fausto Calderazzo in recognition of his outstanding contributions to organometallic chemistry.

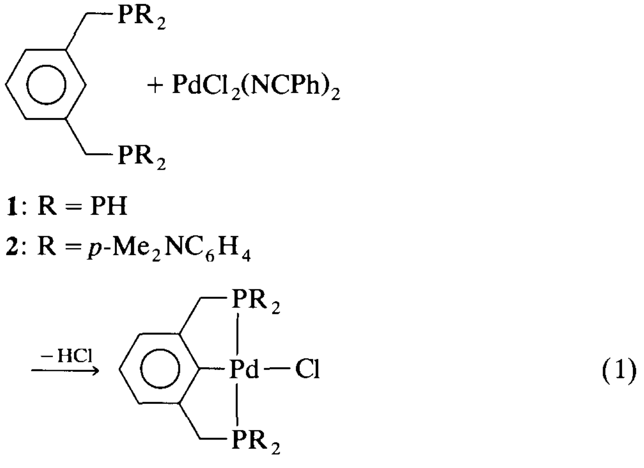
* Corresponding author.

SSDI 0022-328X(94)00027-1

system allows us to vary the electronic characteristics at the metal center without changing the steric interactions in the system. The strategy was to produce the olefin complex from the Pd(II)–halide precursor complex by halide abstraction, and then to study the reactions of the Pd(II)–olefin complex with various nucleophiles.

2. Results and discussion

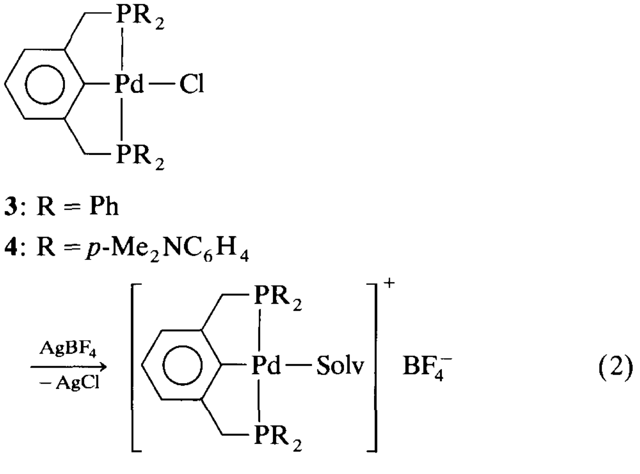
The reaction of 1,3-bis(diphenylphosphino)xylene (dppxH) (**1**) with $PdCl_2(NCPh)_2$ in 2-methoxyethanol at 150°C followed by recrystallization of the crude product from CH_2Cl_2 provides a simple route to the terdentate complex (dppx)PdCl (**3**). Analogously, the dimethylanilino-substituted bisphosphine 1,3-bis(di(*p*-dimethylaniline)phosphino)xylene (dappxH) (**2**) reacts with $PdCl_2(NCPh)_2$ in CH_2Cl_2 to give (dappx)PdCl (**4**).



1: R = PH
2: R = *p*-$Me_2NC_6H_4$
(1)
3: R = Ph
4: R = *p*-$Me_2NC_6H_4$

Chloroform-d_1 solutions of **3** and **4** exhibit a single resonance in the ^{31}P NMR spectrum, at δ 34.6 and δ 31.5, respectively. The crystal structure of **3**, unexpectedly obtained by recrystallization of the dimeric hydride complex {[(dppx)Pd]$_2$(μ-H)}, was recently determined by Gorla et al. [5]. It shows the two phosphines to be in a *trans* disposition at the Pd center, and ^{31}P NMR studies indicate that this geometry is maintained in solution. The ^1H NMR spectrum of **4** shows all NMe_2-groups to be equivalent (δ 2.94). Similarly, only one triplet is displayed for the protons of the methylene groups (CH_2P) of **4**, which is shifted upfield with respect to that of **3**, reflecting the shielding effect of the strongly electron donating *p*-NMe_2-groups.

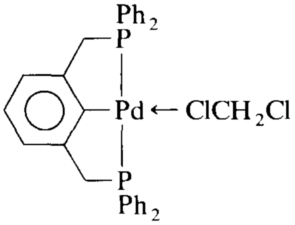
The reaction of **3** and **4** with $AgBF_4$ in CH_2Cl_2 or THF leads cleanly to the ionic complexes $[(dppx)Pd\text{-}solv]^+[BF_4]^-$ (**5**) and $[(dappx)Pd\text{-}solv]^+[BF_4]^-$ (**6**) (Eq. 2). (solv = CH_2Cl_2 or THF).



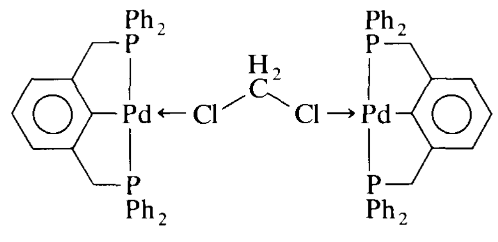
3: R = Ph
4: R = *p*-$Me_2NC_6H_4$
(2)
5: R = Ph
6: R = *p*-$Me_2NC_6H_4$

This reaction can be conveniently monitored by ^{31}P NMR spectroscopy. The signal from the starting complex **3** at δ 34.6 disappears and a new signal attributable to **5** appears further downfield, at δ 40.2 at 0°C, and δ 41.2 at room temperature (solv = $CH_2Cl_2/CDCl_3$). Expectedly, this signal exhibits solvent dependence (dioxane: δ 37.2; acetone: δ 46.2; THF: δ 38.6). Analogously, the chloride in **4** can be abstracted by Ag^+ or Tl^+ to give the ionic complex **6**, which exhibits a single ^{31}P resonance at δ 39.4 (solv = THF). A similar Pd(II) cation with an aliphatic chelating tridentate bisphosphine framework, was obtained by Seligson and Trogler [6] by protonolysis of (d^{t}bpp)PdMe with $[NHMe_3]^+$ and $[NH_2Et_2]^+$ to give [(d^{t}bpp)Pd]$^+$.

In order to confirm that the BF_4^- is not bound to the metal center, but rather that the solvent is coordinating to that center, we undertook a low temperature NMR study of **5**. The NMR signal shows a temperature-dependent behavior similar to that observed by Trogler for [(d^{t}bpp)Pd]$^+$[BF$_4$]$^-$. A solution of **5** in $CH_2Cl_2/CDCl_3$ (9:1), introduced into the spectrometer precooled to −70°C, showed instead of the singlet, two intense signals (δ 41.5 and 39.6) with an integration ratio of 1:1 and three significantly less intense singlets (δ 40.0, 39.2 and 38.5). When the solution is warmed to −30°C the five signals collapse into two signals, a broad signal at δ 40.8 and a sharp, less intense, signal at δ 39.8. Further warming to 0°C causes further collapse of these two signals, to give a single sharp signal at δ 40.2. This process is reversible down to −30°C, but further cooling leads to crystallization of at least one of the species present in solution. The presence of [(dppx)Pd]$^+$, involving three-coordinate Pd with a vacant coordination site is unlikely in the presence of donors such as CH_2Cl_2, $CDCl_3$ and BF_4^-. We suggest that there is coordination also of CH_2Cl_2 to [(dppx)Pd]$^+$ through the lone pairs of the Cl atoms as depicted in **A**. We can also envisage the presence of a CH_2Cl_2-bridged complex **B**.



A



B

Likewise $CDCl_3$, present as the deuterium lock for the NMR spectra, will coordinate to the $[(dppx)Pd]^+$-cation, giving rise to up to three resonances (analogous to **A** and **B**: terminal, doubly-bridging, triply-bridging). At higher temperatures, association and dissociation of the coordinated solvent (CH_2Cl_2 or $CDCl_3$) is too fast on the ^{31}P NMR time scale, causing the signals to collapse at 0°C into the single resonance at δ 40.2 (δ 41.2 at room temperature). The variable temperature ^{19}F NMR data provide no evidence to suggest coordination of BF_4^- to the $[(dppx)Pd]^+$-cation in solution, such as that proposed by Seligson and Trogler for $[(d^tbpp)Pd^+$ [6].

Addition of two equivalents of norbornene to a CH_2Cl_2 solution of **5** causes the immediate disappearance of the resonance at δ 41.2 and the appearance of one at δ 51.1. We assign this resonance to the complex $[(dppx)Pd\text{-norbornene}]^+$ (**7**). This assignment is confirmed by the ^1H NMR spectrum of the reaction solution, which shows five new broad resonances (δ 4.84 ($w_{1/2} = 64$ Hz), 2.34 ($w_{1/2} = 69$ Hz), 1.79 ($w_{1/2} = 60$ Hz), 1.24 ($w_{1/2} = 60$ Hz), 0.59 ($w_{1/2} = 100$ Hz)) in addition to those of the free norbornene. The signals from the free norbornene are significantly broadened ($w_{1/2}$ ca. 20–35 Hz), suggesting an exchange between free olefin and the solvent complex **5** and complex **7** which has the olefin coordinated to the Pd center, according to Eq. (3).

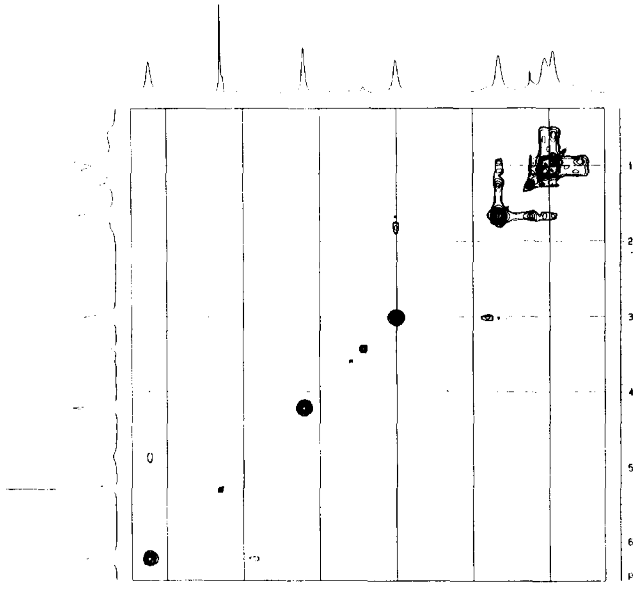
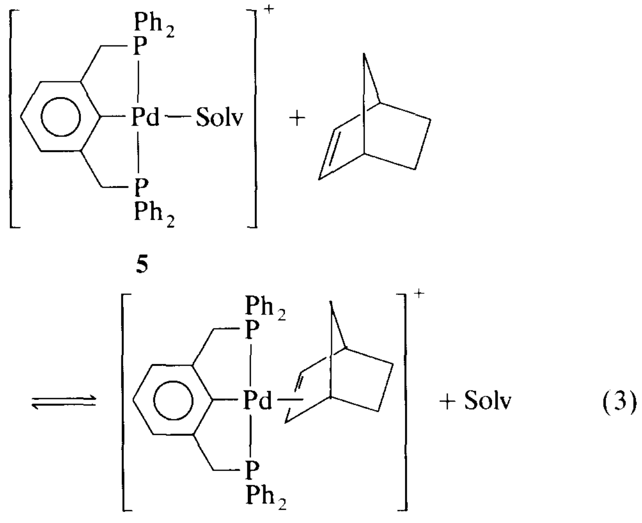


Fig. 1. NOESY spectrum of **7** in $CDCl_3$ in the presence of free THF (20°C, $\tau_{mix} = 0.1$ s).



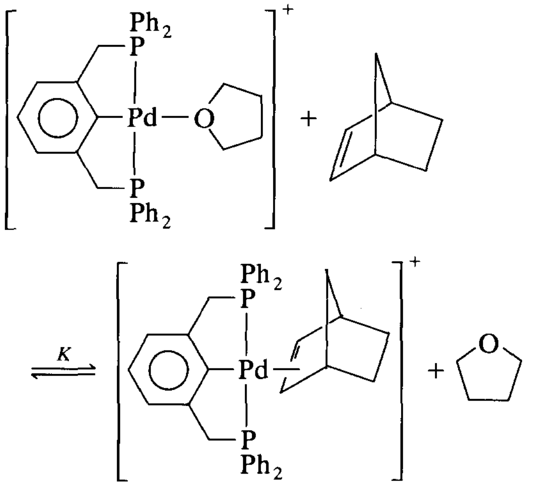
5

7

(3)

A NOESY experiment at room temperature confirms the existence of this equilibrium (Fig. 1). The signal due to the olefinic protons of the free norbornene (δ 6.14) and the broad signal at δ 4.84 exhibit a cross peak, allowing the broad signal to be unequivocally attributed to the two H atoms of the olefinic part of the norbornene coordinated to the Pd center. This assignment is in accordance with the trend that the proton resonances of coordinated olefins are shifted upfield with respect to those for the parent olefin. Similarly, the other signals of the free norbornene can be matched with their respective upfield-shifted counterparts of the coordinated olefin by their cross peaks in the NOESY spectrum.

If the reaction of **5** with norbornene is carried out in THF, the solution shows two distinct broad signals because of **7** at δ 51.1 ($w_{1/2} = 122$ Hz) and $[(dppx)Pd\text{–}THF]^+$ at δ 38.6 ($w_{1/2} = 214$ Hz). The ^1H NMR spectrum shows the characteristic bands resulting from free (3.402, α-H; 1.607, β-H) and coordinated THF (3.730, α-H; 1.834, β-H) and free (δ 6.297, olefinic H) and coordinated olefin (δ 4.909, olefinic H). The equilibrium constant K = 0.17 for the process (Eq. 4) was obtained by integration of the signals from the coordinated and free THF and olefin.



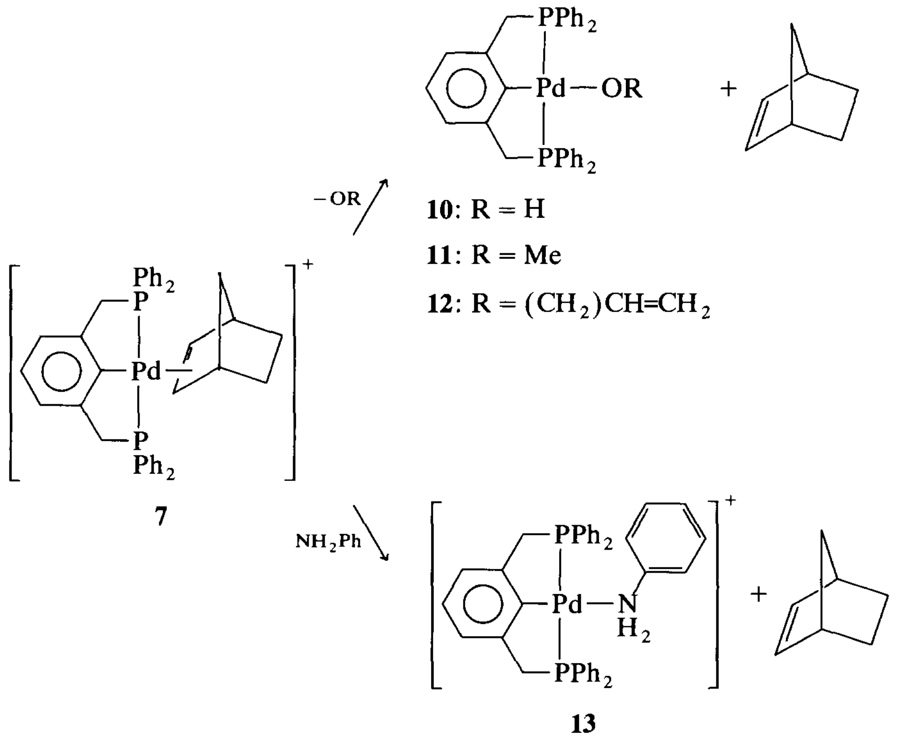
(4)

As can be seen by the shift of the equilibrium to the left, the Pd-olefin interaction is weak. Similarly, an equilibrium was observed for the reaction of **6** with norbornene in THF, again indicating that the interaction is weak (K = 0.41). Two broad signals are observed in the ^{31}P NMR spectrum because of [(dappx)Pd-norbornene]$^+$ (**8**) at δ 39.65 ($w_{1/2}$ = 56 Hz) and the THF adduct of **6** at δ 33.35 ($w_{1/2}$ = 115 Hz) (integration ratio of 1:1). An increase of electron density at the Pd center, caused by the greater electron-release by the phosphine, enhances the π-backbonding component of the Pd–olefin bond, underlining the importance of π-backbonding in this system.

Monitoring of the ^{31}P NMR spectrum of the reaction of **5** with ethylene (80 psi) carried out in CH_2Cl_2 at room temperature in a 5 mm high-pressure NMR tube shows the consumption of the starting material and the appearance of a single new resonance at δ 50.7, probably because of the ethylene π-complex [(dppx)Pd(η^2-CH_2=CH_2)]$^+$ (**9**). All attempts to isolate one or more of the olefin adducts in a pure form or to grow crystals suitable for single crystal X-ray crystallography failed, and the only species isolated was the starting material **5**.

2.1. Reaction of 5 with nucleophiles

Rather unexpectedly, the reaction of **7** with the mildly basic K_2CO_3/H_2O resulted in displacement of the olefin and formation of (dppx)PdOH **10** as the only product. There was no indication of nucleophilic attack of the OH^- on the olefin. Complex **10** was independently prepared by the addition of solid KOH to a THF solution of **5** at room temperature followed by extraction of the product with benzene, by analogy with the method reported for the preparation of (dppx)PtOH, by Bennett et al. [7]. A C_6D_6 solution of **10** exhibits a single resonance in the ^{31}P NMR spectrum at δ 33.4 confirming the expected *trans* arrangement of the chelating dppx around the Pd center. The signal from the four protons of the ligand's methylene groups at δ 3.50, shows coupling to the two equivalent phosphorus, giving rise to a quasitriplet ($^2J_{HP}$ = 4.7 Hz). A triplet at δ 0.92 (^2J = 6.8 Hz) in the ^{1}H NMR spectrum is assigned to the hydroxy proton. The position of this signal and the $^3J_{PH}$ agree well with that observed for the analogous Pt complex (dppx)PtOH (δ 0.21, $^3J_{PH}$ = 5.2 Hz). Other square planar bisphosphine Pt(II)- and Pd(II) hydroxide complexes exhibit reso-



10: R = H

11: R = Me

12: R = $(CH_2)CH$=CH_2

7

13

(5)

nances in the range of δ −2.5 to +1.5 with *cis* $^3J_{PH}$ in the range of 4.0 to 6.9 Hz [8]. Analogous L_nPdOH and L_nPtOH complexes have similar ^1H chemical shifts [8b]. A broad uncharacteristic feature at 3370 cm^{-1} in the IR spectrum is assigned to the OH-stretching vibration, which is probably broadened as a result of extensive hydrogen bonding of the hydroxide in the solid state. The reaction of **7** with NaOMe in THF allows the isolation of (dppx)PdOMe **11** as a white solid. **11** was also obtained by the reaction of **5** with NaOMe. **11** exhibits a single ^{31}P NMR resonance at δ 29.65, slightly upfield shifted from that for **10**. The ^1H NMR spectrum exhibits a virtual triplet (CH_2P group) at δ 3.53 ($^2J_{HP}$ = 4.4 Hz) and a singlet at δ 3.42 (OCH_3 group).

The position of the hydroxide resonance for other square planar bisphosphino Pt(II) alkyl(hydroxides) is very variable, and can range from δ 2.00 for *trans*-$Pt(OMe)(CF_3)(PPh_3)_2$ [8a] to δ 3.92 for (dppe)-Pt(Et)(OMe) [9]. Coupling to the *cis*-phosphines is observed only in some special cases and is generally small (less than 1 Hz) [10]. The benzene-soluble complex (dppx)Pd–$O(CH_2)_4CH{=}CH_2$ (**12**), was obtained similarly by the reaction of **5** with LiO–$(CH_2)_4CH{=}CH_2$ in THF or from **11** by reaction with the free alcohol 1-hexen-5-ol. β-H elimination, common for alkoxide complexes having a more flexible ligand framework [11], is not observed for the more rigid tridentate (dppx)Pd–alkoxide complexes **11** and **12**. This observation is consistent with theoretical predictions by Thorn and Hoffmann [12] that β-H elimination proceeds via a three-coordinate 14-electron Pd(II) intermediate, rather than directly from the four-coordinate 16e complex. Complex **12** exhibits a single resonance at δ 33.44, in the same region as the other two alkoxide complexes **10** and **11**. The protons of the α-CH_2 group appear as a triplet, which is shifted upfield by 0.12 ppm with respect to the signal from the free alcohol, indicating coordination of the alkoxide. However, the splitting is not caused by coupling to the two phosphines of the ligand, but rather by that to the adjacent CH_2-group. This was confirmed by a $^1H\{^{31}P\}$ experiment, which showed that there was no collapse of the triplet upon phosphorus decoupling. Similarly, the methoxide protons of **11** do not show any coupling to the phosphorus. The ^{13}C NMR spectrum shows two olefinic signals, at positions very close to those for the free alcohol and the alkoxide anion (δ 139.64 β-C and δ 115.37 α-C). Furthermore, in the ^1H NMR spectrum, the signals from the olefinic protons are at positions similar to those from the free alkoxide and free alcohol. This suggests that the olefin part of the molecule is dangling rather than occupying a possible fifth coordination site on the Pd center, though the latter cannot at present be excluded. We have no evidence to suggest the formation of a product resulting from an intramolecular olefin insertion into the Pd–O bond; this is not too surprising because observed examples of olefin insertion into M–O bonds are restricted to highly activated olefins, such as acrylonitrile and perfluorinated olefins [13].

Addition of the weak nucleophile aniline to a THF solution of **5** results in the liberation of norbornene and the formation of $[(dppx)PdNH_2Ph]^+(BF_4)^-$ **13**, which crystallizes as a 1:1.5 solvate from CH_2Cl_2 in the form of colorless needles. The spectroscopic features of **13** are fully compatible with retention of the geometric integrity of the (dppx)Pd-core. In contrast, Trogler's $[(d^tbpp)Pd]^+$ prepared by protonolysis with $[NHMe_3]^+$ and $[NH_2Et_2]^+$, does not take up the amines [6], but instead interacts with solvent molecules. The differences in the coordination behavior between Trogler's $[(d^tbpp)Pd]^+$ and $[(dppx)Pd]^+$ are of steric origin. The steric congestion in the $[(dppx)Pd]^+$ cation is less than that in $[(d^tbpp)Pd]^+$, and the cone angle of NH_2Ph (111°) is smaller than those of NMe_3 (132°) and $NHEt_2$ (125°) [14]. Both factors favor coordination of the amine in the case of $[(dppx)Pd]^+$ giving **13**, but prevent coordination of amine to $[(d^tbpp)Pd]^+$.

2.2. Structural studies of 13

Although the poor quality of the crystal structure rules out detailed discussion, we will comment on some key features. An ORTEP view of the cationic complex $[(dppx)Pd(NH_2Ph)]^+$ is shown in Fig. 2. The atom coordinates are given in Table 1, and selected bond distances and angles in Table 2. In keeping with the

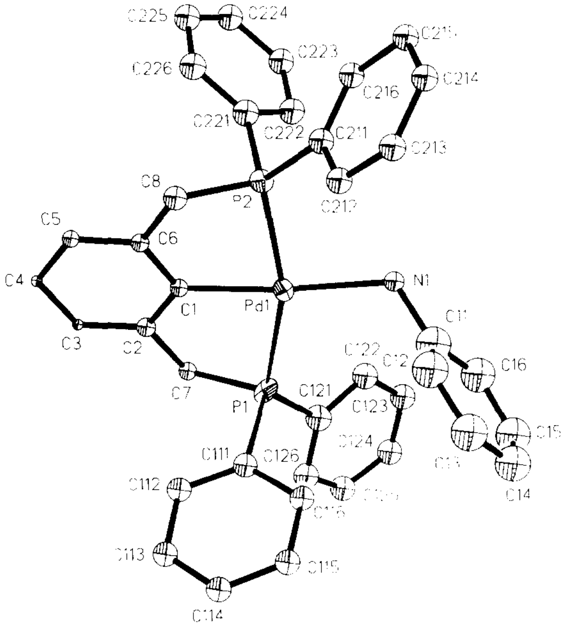


Fig. 2. ORTEP [20] drawing of the cation $[(dppx)PdNH_2Ph]^+$.

solution studies, in the cation there is the expected tetrahedrally distorted square planar coordination environment around the Pd center, commonly observed in similar Pt(II) complexes [5,7,16]. The phosphines are in a *trans* arrangement with a P(1)–Pd–P(2) angle of 160.8 (3)°. This angle is rather small compared with those for the other three structurally characterized Pd(II) systems having a terdentate bisphosphine ligand system, such as the (dppx)PdCl (162.0 (1)°) [5] ($\mathrm{d^tbpp}$)PdMe (162.0 (1)°) [6] and the cationic [($\mathrm{d^tbpp}$)Pd(OH_2)]$^+$ (167.1 (1)°) [6], reflecting the fact that, in addition to the geometric strain imposed by the two five-membered rings formed upon chelation, the steric congestion about the metal center is increased by the coordination of the aniline. The only way to relieve some of this steric pressure other than by tetrahedral distortion, which is observed in all three cases, is to reduce the P–Pd–P angle. The Pd–N(1) bond length of 2.156 (24) Å is within the binding range established for Pd(II)–amine complexes by Seligson and Trogler [14].

Table 1
Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients for **13**

Atom	*x*	*y*	*z*	*U*
Pd(1)	2304(2)	1106(1)	4813(1)	17(1)
P(1)	3571(8)	1143(5)	5865(4)	22(3)
P(2)	1247(8)	684(5)	3809(4)	18(3)
N(1)	1849(22)	2186(13)	4563(11)	23(11)
C(111)	2698(28)	978(16)	6517(14)	23(4)
C(112)	2768(27)	349(16)	6835(14)	23(4)
C(113)	2040(26)	274(16)	7366(14)	23(4)
C(114)	1306(28)	809(16)	7532(15)	23(4)
C(115)	1155(28)	1431(16)	7195(15)	23(4)
C(116)	1860(27)	1539(16)	6678(15)	23(4)
C(121)	4763(30)	1815(17)	6153(17)	30(4)
C(122)	5046(30)	2292(17)	5690(16)	30(4)
C(123)	6006(29)	2831(17)	5912(17)	30(4)
C(124)	6693(31)	2823(17)	6546(16)	30(4)
C(125)	6376(30)	2314(16)	6960(17)	30(4)
C(126)	5428(29)	1814(17)	6795(16)	30(4)
C(211)	−145(26)	1135(18)	3357(14)	22(4)
C(212)	−1209(26)	1279(15)	3661(14)	22(4)
C(213)	−2340(28)	1641(15)	3297(15)	22(4)
C(214)	−2380(29)	1849(15)	2677(15)	22(4)
C(215)	−1294(27)	1720(6)	2345(15)	22(4)
C(216)	−195(28)	1339(15)	2733(15)	22(4)
C(221)	2270(29)	484(17)	3219(15)	28(4)
C(222)	3240(27)	1004(17)	3135(14)	28(4)
C(223)	3995(29)	863(16)	2662(15)	28(4)
C(224)	3893(29)	247(17)	2319(15)	28(4)
C(225)	2999(29)	−223(17)	2408(15)	28(4)
C(226)	2196(30)	−117(17)	2864(15)	28(4)
C(11)	1371(35)	2615(19)	5064(18)	47(5)
C(12)	177(34)	2503(20)	5237(17)	47(5)
C(13)	−290(35)	2900(19)	5703(18)	47(5)
C(14)	494(34)	3460(19)	5991(18)	47(5)
C(15)	1646(34)	3575(19)	5822(18)	47(5)
C(16)	2103(34)	3197(19)	5341(17)	47(5)
F(1)	2079(10)	7688(8)	1499(8)	53(6)
F(2)	816(15)	8541(6)	1629(8)	61(6)
F(3)	169(14)	7491(8)	1717(8)	70(7)
F(4)	343(17)	7893(10)	778(6)	114(10)
B(1)	852(10)	7903(6)	1406(5)	68(17)
C(1)	2625(26)	64(15)	4956(13)	13(8)
C(2)	3728(27)	−181(16)	5434(14)	15(9)
C(3)	3965(25)	−890(13)	5510(13)	5(8)
C(4)	3165(24)	−1375(13)	5105(13)	5(8)
C(5)	2083(25)	−1096(16)	4621(13)	12(7)
C(6)	1832(26)	−411(16)	4559(14)	13(8)
C(7)	4587(26)	345(15)	5855(14)	14(8)
C(8)	670(28)	−153(16)	4067(14)	22(9)

Table 2
Selected bond distances (Å) and angles (°) for **13**

Distances			
Pd(1)–P(1)	2.317(8)	Pd(1)–P(2)	2.302(8)
Pd(1)–N(1)	2.156(24)	Pd(1)–C(1)	2.031(28)
P(1)–C(111)	1.790(33)	P(1)–C(121)	1.798(32)
P(1)–C(7)	1.852(30)	P(2)–C(211)	1.777(28)
P(2)–C(221)	1.803(35)	P(2)–C(8)	1.821(32)
N(1)–C(11)	1.481(46)	C(1)–C(2)	1.435(36)
C(1)–C(6)	1.381(38)	C(2)–C(3)	1.380(39)
C(3)–C(4)	1.405(34)	C(4)–C(5)	1.450(34)
C(6)–C(5)	1.334(43)		
Angles			
P(1)–Pd(1)–P(2)	160.8(3)	P(1)–Pd(1)–N(1)	104.8(6)
P(2)–Pd(1)–N(1)	94.3(6)	P(1)–Pd(1)–C(1)	81.1(8)
P(2)–Pd(1)–C(1)	79.8(8)	N(1)–Pd(1)–C(1)	174.1(9)
C(111)–P(1)–C(7)	103.3(14)	C(121)–Pd(1)–C(7)	104.0(14)
C(111)–P(1)–C(121)	106.5(15)	Pd(1)–P(1)–C(7)	100.5(9)
C(211)–Pd(2)–C(8)	107.8(14)	C(221)–P(2)–C(8)	106.2(15)
C(211)–P(2)–C(221)	105.1(14)	Pd(1)–P(2)–C(8)	99.8(9)
Pd(1)–N(1)–C(11)	116.6(20)	P(1)–C(7)–C(2)	106.6(18)
P(2)–C(8)–C(6)	103.1(19)	C(1)–C(2)–C(3)	119.9(24)
C(1)–C(6)–C(5)	120.4(24)	C(2)–C(3)–C(4)	120.5(22)
C(2)–C(1)–C(6)	119.7(25)	C(3)–C(4)–C(5)	117.1(23)
C(4)–C(5)–C(6)	122.3(24)		

The cation is strongly associated with the BF_4^- counterion (Fig. 3), having a close F ··· N distance of 2.856 (24) Å, suggesting the presence of hydrogen bonding via a N– ··· F bridge. Such interactions are well-known in the literature for simple ammonia adducts, such as $NH_3 \cdot BF_3$ (d(N-H ··· F) = 3.01 ± 0.03 Å) or inorganic salts like NH_4F (d(N-H ··· F) = 2.69 Å) and NH_4HF_2 (*d*(N-H ··· F) = 2.80 ± 0.03 Å) [17], but are not well-documented for organometallic systems. However, N-H ··· O and O-H ··· O hydrogen bonding has been observed by several groups for alkoxide and amine ligands coordinated to Pd [18].

3. Conclusions

The solvated cations [(dppx)Pd-Solv]$^+$ and [(dappx)-Pd-Solv]$^+$ add norbornene to give the corresponding cationic norbornene complexes. However, our study shows that norbornene is only weakly bound to the metal center, probably owing to the *trans* labilization

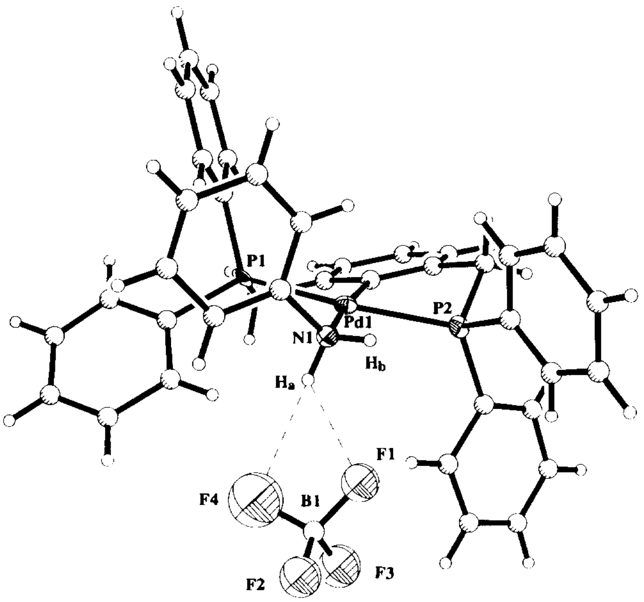


Fig. 3. N–H ··· F hydrogen bonding between the cation [(dppx)-PdNH$_2$Ph]$^+$ and the anion BF$_4^-$ in **13**.

of the carbon of the orthometallated benzene ring. An increase in the electron density on the metal center raises the stability of the Pd–olefin complex, but the olefin is insufficiently activated by the Pd center to allow nucleophilic attack. The reaction with anionic oxygen-based nucleophiles invariably leads to olefin replacement and formation of Pd–alkoxide complexes. The coordination geometry of the (dppx)Pd-moiety is maintained after reaction with nucleophiles. The olefin is replaced even by aniline, leading to the corresponding cationic Pd–anilino complex. The alkoxide complexes are stable towards β-H elimination, because of the non-availability of a vacant coordination site at the Pd center imposed by the rigidity of the ligand framework, in accord with earlier theoretical predictions. No olefin insertion into the Pd–O bond, either intra- or inter-molecular, is observed.

4. Experimental details

4.1. General

4.1.1. Materials

All reactions were carried out under nitrogen in a Vacuum Atmospheres glovebox (DC-882) equipped with a recirculation (MO-40) "Dri Train" or under argon by use of standard Schlenk techniques. All solvents were rigorously dried by refluxing over the appropriate drying agents, and were degassed prior to storage in the glovebox over 4 Å molecular sieves: benzene (Frutarom, Na/benzophenone), toluene (Frutarom, Na/benzophenone), pentane (Merck, Na/benzophenone, tetraglyme), tetrahydrofuran (Biolab, Na/benzophenone), dichloromethane (Frutarom, P_2O_5). Deuterated solvents were purchased from Aldrich, and were degassed and stored over 4 Å molecular sieves in the glove box. $AgBF_4$ (Alfa), $NaPF_6$ (Aldrich), norbornene (Aldrich), and aniline (Aldrich) were used as received. $NaOCH_3$ was prepared from sodium and methanol on an argon Schlenk line. $LiO(CH_2)_4CH{=}CH_2$ was prepared from ^{n}BuLi and $HO(CH_2)_4CH{=}CH_2$ in pentane on an argon Schlenk line. $PdCl_2(NCPh)_2$ was prepared by the published procedure [19].

4.1.2. Spectroscopy

Infrared spectra were recorded as Nujol mulls or as neat films between NaCl plates on a Nicolet MX-1 spectrometer. The ^{1}H, ^{13}C, ^{31}P NMR spectra were recorded at 400.19, 161.9 and 100.6 MHz respectively, on a Bruker AMX 400 NMR spectrometer. The ^{1}H NMR shifts were referenced to the resonance of the residual protons of the solvents. The ^{31}P NMR shifts were referenced to external 85% H_3PO_4 (in D_2O).

4.2. Synthesis of (dappx)PdCl (4)

A pressure flask equipped with a stirring bar, was charged as a solution of dappx (280 mg, 0.432 mmol) in dichloromethane (15 ml), and a solution of $(PhCN)_2PdCl_2$ (151 mg, 0.394 mmol) in 20 ml of dichloromethane was added with stirring. The mixture was kept for 12 h at 120°C, then allowed to cool to room temperature and was filtered and reduced in volume to 10 ml. The crude orange product was precipitated by the addition of 20 ml Et_2O. It was washed with Et_2O (2 × 10 ml) and dried in vacuo to give 218 mg of (dappx) PdCl · CH_2Cl_2. Yield: 63%. Elemental Anal.: Calc. for $C_{41}H_{49}Cl_3N_4P_2Pd$ (MW = 872.59): C, 56.44; H, 5.66. Found: C, 56.37; H, 6.05% ^{31}P{^{1}H} (δ, $CDCl_3$): 31.47 (s). ^{1}H (δ, $CDCl_3$): 7.703 (8H, m, H_{ortho} of PC_6H_4R), 7.019 (2H, d, $J = 7.2$ Hz, H_{meta}), 6.919 (1H, t, $J = 7.2$ Hz, H_{para}), 6.677 (8H, d, $J = 8.4$ Hz, H_{ortho} of PC_6H_4R), 3.830 (4H, vt, $J_{HP} = 4.6$ Hz, CH_2P), 2.942 (s, $N(CH_3)_2$). ^{13}C{^{1}H} (δ, $CDCl_3$): 161.1 (s, C_{ipso}), 152.1 (s, PC_{para}), 149.3 (vt, $J_{CP} = 10.7$ Hz, C_{ortho}), 134.8 (vt, $J_{CP} = 7.4$ Hz, PC_{ortho}), 125.9 (s, C_{para}), 123.4 (vt, $J_{CP} = 11.2$ Hz, C_{meta}), 118.9 (vt, $J_{CP} = 25.0$ Hz, PC_{ipso}), 112.6 (vt, $J_{CP} = 5.4$ Hz, PC_{meta}), 44.3 (vt, $J_{CP} = 14.4$ Hz, PCH_2), 40.8 (s, $N(CH_3)_2$)).

4.3. Variable temperature ^{31}P NMR spectroscopic study of [(dppx)Pd]$^+$[BF$_4$]$^-$ (5)

(dppx)PdCl (46 mg, 0.075 mmol) was dissolved in CH_2Cl_2 (5 ml) and a solution of $AgBF_4$ (15 mg, 0.075 mmol) in 2 ml of CH_2Cl_2 was added. The mixture was stirred for 30 mins, then filtered, and the colorless filtrate was evaporated in vacuo to leave a white solid, which was dissolved in a 9 : 1 mixture of CH_2Cl_2 : $CDCl_3$ for NMR studies.

4.4. *Spectroscopic characterization of $[(dappx)Pd \cdot THF]^+[PF_6]^-$ (**6**)*

A solution of $TlPF_6$ (5 mg, 0.014 mmol) in 5 ml of THF was added to a stirred solution of (dappx)PdCl (11 mg, 0.0135 mmol) in THF (10 ml). The color darkened and a precipitate was formed. After 20 min the mixture was filtered through a cotton pad to give a clear orange-red solution, which was then evaporated to dryness under reduced pressure. The residue was dissolved in $CDCl_3$ for spectroscopic studies.

$^{31}P\{^1H\}$ (δ, $CDCl_3$): 39.42 (s, $[(dappx)Pd \cdot THF]^+$), −143.00 (spt, $J_{PF} = 714$ Hz, PF_6^-). ^1H (δ, $CDCl_3$): 7.470 (8H, m, H_{ortho} of PC_6H_4R), 7.079 (2H, d, $J = 6.8$ Hz, H_{meta}), 7.015 (1H, t, $J = 6.8$ Hz, H_{para}), 6.765 (8H, d, $J = 8.5$ Hz, H_{ortho} of PC_6H_4R), 3.89 (4H, vt, $J_{HP} = 4.6$ Hz, CH_2P), 3.745 (THF), 3.01 (24H, s, $N(CH_3)_2$), 1.851 (THF).

4.5. *Spectroscopic characterization of $[dppxPd\text{-}norbornene]^+[BF_4]^-$ (7)*

To a clear solution of (dppx)PdCl (38 mg, 0.062 mmol) in CH_2Cl_2 (3 ml) was added one of $AgBF_4$ (12 mg, 0.062 mmol) in 2 ml of CH_2Cl_2. The mixture was stirred for 20 mins, during which copious amounts of AgCl separated. The AgCl was removed, and the ^{31}P NMR spectrum of the filtrate showed that there had been complete conversion into $[(dppx)Pd]^+$ ($^{31}P\{^1H\}$(δ, CD_3COCD_3): 41.4. ^1H (δ, CD_3COCD_3): 7.75 (8H, m, H_{ortho} of PC_6H_5), 7.56 (12H, m, H_{meta} and H_{para} of PC_6H_5), 7.16 (2H, d, $^3J_{HH} = 7.4$ Hz, H_{meta}), 7.04 (1H, t, $^3J_{HH} = 7.4$ Hz, H_{para}), 4.21 (4H, t, $^2J_{HP} = 4.7$ Hz, PCH_2). There was no signal from the starting material (dppx)PdCl. To the filtrate were added two equivalents of norbornene (12 mg, 0.127 mmol), and the mixture was stirred for 10 mins, then evaporated to dryness under reduced pressure. The obtained solid was dissolved in $CDCl_3$ for the NMR investigations.

$^{31}P\{^1H\}$(δ, $CDCl_3$): 51.3. ^1H (δ, $CDCl_3$): 7.67 (m, H_{ortho} of PC_6H_5), 7.54 (br, H_{meta} and H_{para} of PC_6H_5), 7.04 (d, $^3J_{HH} = 7.4$ Hz, H_{meta}), 6.93 (t, $^3J_{HH} = 7.3$ Hz, H_{para}), 6.14 (s, br, $w_{1/2} = 28$ Hz, olefinic H of free norbornene), 4.75 (s, br, $w_{1/2} = 64$ Hz, olefinic H of free norbornene), 4.19 (s, br, PCH_2), 2.94 (s, br, $w_{1/2} = 28$ Hz, free norbornene), 1.72 (s, br, $w_{1/2} = 69$ Hz, coord. norbornene), 1.60 (s, br, $w_{1/2} = 30$ Hz, free norbornene), 1.20 (s, br, $w_{1/2}$ ca. 80 Hz), 1.00 (s, br, $w_{1/2} = 35$ Hz, free norbornene), 0.93 (s, br, $w_{1/2} = 32$ Hz, free norbornene), 0.59 (s, br, $w_{1/2} = 100$ Hz, coord. norbornene).

4.6. *Synthesis of (dppx)PdOH (**10**)*

In a modification of the procedure used for the preparation of (dppx)PtOH, a solution of $AgBF_4$ (23 mg) in 2 ml of THF was added to a vigorously stirred solution of (dppx)PdCl (71 mg, 0.115 mmol) in THF (20 ml) contained in an Al-foil-covered vial. After 2 h at room temperature, the mixture was filtered and a solution of NaOH (6 mg, 0.150 mmol) in 0.5 ml of water was added to the filtrate. The mixture was stirred overnight with exclusion of light, and the solvent was then removed in vacuo to leave a yellowish solid. This was redissolved in a minimum amount of THF (2 ml) and the solution was filtered. Addition of diethyl ether (5 ml) caused separation of a solid, which was filtered off to leave a yellow solution, which was evaporated to dryness under reduced pressure to leave a yellow solid.

IR (NaCl, film): 3370 cm^{-1}, br. $^{31}P\{^1H\}$(δ, C_6D_6): 33.42 (s). ^1H(δ, C_6D_6): 8.00 (8H, m, H_{ortho} of PC_6H_5), 7.09 (15H, m, H_{meta} and H_{para} of PC_6H_5 and H_{meta}, H_{para}), 3.50 (4H, vt, $^2J_{HP} = 4.7$ Hz, PCH_2), 0.92 (1H, vt, $^3J_{HP} = 6.8$ Hz, Pd–OH).

4.7. *Synthesis of $(dppx)PdOCH_3$ (11)*

To a solution of $[(dppx)Pd]^+[BF]^-$ prepared in situ from (dppx)PdCl, 29 mmg, 0.047 mmol and $AgBF_4$, 9 mg, 0.046 mmol was added a solution of NaOMe (2 mg, 0.056 mmol) in 2 ml of THF. The mixture was stirred for 10 min and then evaporated to dryness under reduced pressure. The solid residue was extracted with benzene or benzene-d_6 to give a yellow-brown solution, which was evaporated to dryness under reduced pressure to leave a yellow solid.

$^{31}P\{^1H\}$(δ, C_6D_6): 29.65 (s). ^1H(δ, C_6D_6): 8.02–7.95 (8H, m, Ph), 7.11–6.93 (15H, m, Ph), 3.53 (4H, vt, $^2J_{HP} = 4.4$ Hz, PCH_2), 3.42 (3H, s, OCH_3). $^{13}C\{^1H\}$(δ, C_6D_6): 149.86 (vt, $^2J_{CP} = 10.9$ Hz, C_{ortho}), 134.34 (vt, $^1J_{CP} = 20.7$ Hz, PC_{ipso}), 133.98 (vt, $^2J_{CP} = 6.8$ Hz, PC_{ortho}), 131.10 (s, PC_{para}), 129.57 (vt, $^3J_{CP} = 5.0$ Hz, PC_{meta}), 126.38 (s, C_{para}), 123.75 (vt, $^2J_{CP} = 10.7$ Hz, C_{meta}), 50.80 (s, OCH_3), 43.53 (vt, $^2J_{CP} = 14.7$ Hz, PCH_2).

4.8. *Synthesis of $(dppx)PdOCH_2CH_2CH_2CH_2CH{=}CH_3$ (12)*

A solution of $[(dppx)Pd]^+[BF_4]^-$, prepared in situ from (dppx)PdCl (32 mg, 0.052 mmol) and $AgBF_4$ (10 mg, 0.052 mmol), was filtered and a solution of $LiOCH_2CH_2CH_2CH_2CH{=}CH_2$ (5 mg, 0.047 mmol) in THF (2 ml) was added. The yellow solution was stirred for 1 h and then evaporated to dryness under reduced pressure. The residue was extracted with benzene or benzene-d_6 to give a light-yellow solution, from which the solvent was removed to leave a yellow solid.

^{31}P{^{1}H}(δ, C_6D_6): 33.44. ^{1}H(δ, C_6D_6): 8.02–7.97 (8H, m, H_{ortho} of PC_6H_5), 7.10–6.94 (15H, m, H_{meta} and H_{para} of PC_6H_5 and H_{meta} and H_{para}), 5.72 (m, 1H, $CH{=}CH_2$), 4.97 (2H, m, $CH{=}CH_2$), 3.51 (4H, vt, $^2J_{HP} = 4.6$ Hz, PCH_2), 3.29 (2H, t, $^3J_{HH} = 5.9$ Hz, OCH_2), 1.91 (2H, m, CH_2), 1.38 (2H, m, CH_2), 1.29 (2H, m, CH_2). ^{13}C{^{1}H}(δ, C_6D_6): 149.2 (s, C_{ortho}), 139.64 (s, $CH{=}CH_2$), 133.72 (vt, $^2J_{CP} = 6.7$, PC_{ortho}), 133.37 (vt, $^1J_{CP} = 21.2$, PC_{ipso}), 130.83 (s, PC_{para}), 129.20 (vt, $^3J_{CP} = 5.1$, PC_{meta}), 126.35 (s, C_{para}), 123.69 (vt, $^3J_{CP} = 11.5$, C_{meta}), 115.37 (s, $CH{=}CH_2$), 63.8 (s, OCH_2), 43.08 (vt, $^1J_{CP} = 14.4$, PCH_2), 34.18 (s, CH_2), 32.86 (s, CH_2), 26.14 (s, CH_2).

4.9. Preparation of [(dppx)PdNH$_2$Ph]$^+$[BF$_4$]$^-$ (13)

In two parallel experiments (A and B) (dppx)PdCl (16 mg, 0.0259 mmol) was dissolved in 10 ml of THF in vials, which were covered with Al foil. A solution of $AgBF_4$ (6 mg, 0.0308 mmol) was added to each vial and the mixture was stirred for 1 h, then filtered through a cotton plug, and norbornene (50 mg, 0.531 mmol) was added to each filtrate. Aniline (50 mg, 0.531 mmol) was added to one solution. Both solutions were stirred overnight, and the solvent was then removed from each. The residual solids were washed with pentane (2 × 10 ml) to remove the excess of aniline and norbornene, and were then dried in vacuo. Both were dissolved in $CDCl_3$ for NMR studies.

4.9.1. A (norbornene added only)

^{31}P{^{1}H} (δ, $CDCl_3$): 51.2 ($w_{1/2} = 122$ Hz) [(dppx)Pd-norbornene]$^+$, 38.6 ($w_{1/2} = 214$ Hz) [(dppx)Pd-THF]$^+$. ^{1}H (δ, $CDCl_3$): 6.297 (vbr, olefinic H, free norbornene), 4.909 (vbr, olefinic H, coord. norbornene), 3.730 (α-H, coord. THF), 3.402 (α-H, free THF), 1.834 (β-H, coord. THF), 1.607 (β-H, free THF).

*4.9.2. **B** (norbornene and aniline added)*

The product crystallized from the reaction solution as colorless needles, one of which was used for the X-ray diffraction study. The yield was in the range 70–82%. Scaling up of the reaction resulted in an increase in the yield.

^{31}P{^{1}H} (δ, $CDCl_3$): 41.20. ^{1}H (δ, $CDCl_3$): 7.487 (20H, m, *o*-, *m*-, *p*-H of $P(C_6H_5)_2$), 7.153 (2H, t, $J_{HH} = 7.5$ Hz, *m*-H of NC_6H_5), 7.028 (2H, d, $J_{HH} = 7.5$ Hz, *m*-H of Pd-C_6H_3), 6.962 (1H, t, $J_{HH} = 7.5$ Hz, *p*-H of PdC_6H_3), 6.830 (1H, t, $J_{HH} = 7.2$ Hz, *p*-H of NC_6H_5), 6.770 (2H, d, $J_{HH} = 6.2$ Hz, *o*-H of NC_6H_5), 5.021 (2H, br, NH_2), 3.951 (4H, t, $J_{HH} = 4.5$ Hz). ^{13}C{^{1}H} (δ, $CDCl_3$): 156.40 (s, C_{ipso}), 147.65 (vt, $^2J_{CP} = 9.4$ Hz, C_{ortho}), 143.27 (br, NC_{ipso}, $H_2NC_6H_5$), 133.63 (vt, $^2J_{CP} = 6.8$ Hz, PC_{ortho}), 131.60 (vt, $^1J_{CP} = 34.8$ Hz, PC_{ipso}), 132.32 (s, PC_{para}), 130.32 (vt, $^3J_{CP} = 5.0$ Hz, PC_{meta}), 129.85 (br, C_{ortho}, $H_2NC_6H_5$), 127.76 (s, C_{para}), 124.54 (vt, $^3J_{CP} = 10.9$ Hz, C_{meta}), 120.84 (br, C_{para}, $H_2NC_6H_5$), 115.93 (br, C_{meta}, $H_2NC_6H_5$), 42.96 (vt, $^1J_{CP} = 14.7$ Hz, PCH_2).

Table 3
Crystal data for [(dppx)PdNH$_2$Ph][BF$_4$]·1.5 CH$_2$Cl$_2$ and details of data collection and refinement

Formula	$C_{38}H_{34}BF_4P_2PdN \cdot 1.5\ CH_2Cl_2$
Fw	873.7
Space group	$P2_1/n$
a, Å	10.293 (2)
b, Å	19.108 (4)
c, Å	20.743 (4)
β, deg	101.09 (3)
V, Å^3	4003.2 (14)
Z	4
d_{calc}, g cm^3	1.447
Crystal size, mm	0.10 × 0.05 × 0.40
F(000)	1756.68
μ (Mo–Kα), cm^{-1}	0.771
Data collection instrument	CAD4
Radiation (monochromated in incident beam)	Mo–Kα
Orientation reflections: no.	2
Temp, K	113
Scan method	Ω
Data collection range (2θ), deg	2–36 ($-8 < h < 8$; $-1 < k < 16$; $-1 < l < 18$)
No. of data collected, unique, total observations	2904, 2744, 1467 ($F > 4\sigma(F)$)
No. of parameters refined	233
R, R_w	8.60, 10.16
R, R_w (all data)	16.00, 12.78
Goodness of Fit	1.43
Largest peak/hole, e Å^3	0.91, −1.36

4.10. X-ray structural study of [(dppx)PdNH$_2$Ph]$^+$ [BF$_4$]$^-$·1.5 CH$_2$Cl$_2$ (13)

Pertinent crystallographic information is summarized in Table 3. Well-formed colorless needles of [(dppx)PdNH$_2$Ph][BF$_3$]·1.5 CH_2Cl_2 were obtained from CH_2Cl_2 by slow evaporation of the solvent. A crystal of dimensions ca. 0.01 × 0.05 × 0.4 mm was mounted on a glass fiber by use of silicone grease, and was placed in the cold stream of the CAD4 diffractometer. Cell parameters were obtained by indexing 20 carefully centered reflections. Systematic absences defined the space group as $P2_1/n$ ($h00$: $h \neq 2n$; $0kl$: $k + l \neq 2n$) Monitoring of two standard reflections every 120 min revealed no decay of the crystal. The data were corrected for Lorentz and polarization effects. The SHELXTL program package installed on a Silicon graphics workstation was used for all calculations. Scattering factors and corrections for anomalous dispersion were taken from the International Tables for Crystallography [20].

The Pd atom was located in the Patterson map. The structure was expanded using Fourier methods and refined by full-matrix least-squares refinement. The Pd, P, N and Cl atoms (Cl1, Cl2, Cl3) were refined with anisotropic temperature factors. All other atoms were refined with isotropic temperature factors. The hydrogen atoms were included in the structure factor calculations at a later stage using a riding model with d(C–H) = 0.98 Å and $U_{iso} = 1.2U_{iso}$ for the bonded carbon atoms and d(N–H) = 0.85 Å. The phenyl rings of the PPh_2- and NH_2Ph-groups were refined as regular hexagons. The orthometallated xylene was refined without any constraints.

The BF_4^- anion was restrained to be a tetrahedron with d(B–F) = 1.31 Å in the initial least-squares cycles (final, 1.307 (7) Å) because of a disorder. The two positions for the dichloromethane molecules were disordered. One of them had a 50% occupancy, and the other 100%. In the final difference map, several features of about 1 e $Å^3$ appeared around the disordered dichloromethane molecules, but could not be interpreted in a chemically meaningful way. The illustrations were drawn with ORTEP-II [15].

Complete lists of bond lengths and angles, and tables of thermal parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

This research was supported under Grant No. TA-MOU-CA 13041, Program in Science and Technology Cooperation, U.S. Agency for Internal Development. We thank the MINERVA Foundation, Munich, F.R. Germany for a post-doctoral fellowship to H.-B.K.

References

[1] (a) R.F. Heck, *Palladium Reagents in Organic Syntheses*, Academic Press, New York, 1985.

[2] (a) J.K. Stille and R. Divakaruni, *J. Am. Chem. Soc., 100* (1978) 1303–1304; (b) N. Gragor and P.M. Henry, *J. Am. Chem. Soc., 103* (1981) 681–682; (c) K. Zaw, M. Lautens and P.M. Henry, *Organometallics, 2* (1983) 197–199.

[3] (a) D.A. White, *J. Chem. Soc. (A)* (1971) 145–147; (b) J.K. Stille and D.E. James, *J. Organomet. Chem., 108* (1976) 401–408.

[4] (a) O. Eisenstein and R. Hoffmann, *J. Am. Chem. Soc., 103* (1981) 4308–4320; (b) A.D. Cameron, V. Smith jr. and M.C. Baird, *J. Chem. Soc., Dalton Trans.*, (1988) 1037–1043.

[5] F. Gorla, L.M. Venanzi and A. Albinati, *Organometallics 14* (1994) 43–54.

[6] A.L. Seligson and W.C. Trogler, *Organometallics, 12* (1993) 738–743.

[7] M.A. Bennett, H. Jin and A.C. Willis, *J. Organomet. Chem., 451* (1993) 249–256.

[8] (a) R.A. Michelin, M. Napoli and R. Ros, *J. Organomet. Chem., 175* (1979) 239; (b) T. Yoshida, T. Okano and S. Otsuka, *J. Chem. Soc., Dalton Trans.*, (1976) 993–999.

[9] H.E. Bryndza, J.C. Calabrese, M. Marsi, D.C. Roe, W. Tam and J.E. Bercaw, *J. Am. Chem. Soc., 108* (1986) 4805–4813.

[10] R. Ros, R.A. Michelin, R. Bataillard and R. Roulet, *J. Organomet. Chem., 161* (1978) 75–90.

[11] H.E. Brynzda and W. Tam, *Chem. Rev. 88* (1988) 1163–1188.

[12] (a) D.L. Thorn and R. Hoffmann, *J. Am. Chem. Soc., 100* (1978) 2079–2090; (b) N. Koga, S. Obara, K. Kitaura and K. Morokuma, *J. Am. Chem. Soc., 107* (1985) 7109–7116.

[13] (a) H.E. Bryndza, J.C. Calabrese and S.S. Wreford, *Organometallics, 3* (1984) 1603–1604; (b) H.E. Bryndza, *Organometallics, 4* (1985) 406–408.

[14] A.L. Seligson and W.C. Trogler, *J. Am. Chem. Soc., 113* (1991) 2520–2527.

[15] C.K. Johnson, *ORTEP-II*, *Report ORNL-5138*, Oak Ridge National Laboratory, Park Ridge, TN 1976; USA.

[16] (a) F. Gorla, A. Togni, L.M. Venanzi, A. Albinati and F. Lianza, *Organometallics, 13* (1994) 1607–1616; (b) A. Albinati, F. Lianza, P.S. Pregosin and B. Müller, *Inorg. Chem., 33* (1994) 2522–2526; (c) M. Ito, M. Ebihara and T. Kawamura, *Inorg. Chim. Acta, 218* (1994) 199–202.

[17] G.C. Pimentel and A.L. McClellan, *The Hydrogen Bond*, W.H. Freeman & Co.; San Francisco, 1960.

[18] (a) H.E. Brynzda and W. Tam, *Chem. Rev., 88* (1988) 1163–1188; (b) Y.-J. Kim, K. Osakada, A. Takenaka and A. Yamamoto, *J. Am. Chem. Soc., 112* (1990) 1096, and references cited therein; (c) P.L. Alsters, P.J. Baesjou, M.D. Janssen, H. Kooijman, A. Sicherer-Roetman, A.L. Spek and G. van Koten, *Organometallics, 11* (1992) 4124–4135.

[19] (a) M.S. Kharash, R.C. Seyler and F.R. Mayo, *J. Am. Chem. Soc., 60* (1938) 882–884; (b) H. Dietl, H. Reinheimer, J. Moffat and P.M. Maitlis, *J. Am. Chem. Soc., 92* (1970) 2276–2285.

[20] *International Tables for Crystallography*, Vol. 4, Kynoch, Birmingham, UK.