Olefins Coordinated at a Highly Electrophilic Site − Dicationic Palladium(II) Complexes and Their Equilibrium Reactions with Nucleophiles

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Dedicated to Professor Paolo Corradini on the occasion of his 70th birthday

Keywords: Palladium / Alkene complexes / Nucleophilic additions / Tridentate ligands / Aminations

Dicationic olefin palladium(II) complexes [Pd(PNP)(olefin)]$(BF_4)_2$ [olefin = ethylene, propene, styrene, (*Z*)-2-butene, (*E*)-2-butene, norbornene; PNP = 2,6-bis(diphenylphosphanylmethyl)pyridine] have been prepared and characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. The coordinated double bond in these complexes is strongly electrophilic, and easily adds a variety of nucleophiles NuH (H_2O, MeOH, aliphatic and aromatic amines). This reaction competes with olefin displacement in a rapidly reversible equilibrium process, as a result of which the addition products can also be obtained starting from the substituted compounds [Pd(PNP)(NuH)]$(BF_4)_2$ and the appropriate olefin. Equilibrium constants for the addition and substitution reactions have been determined in a number of cases. Proton abstraction from [Pd(PNP)(CHRCHR′NuH)]$^{2+}$ by $NaHCO_3$ quantitatively drives the equilibrium to β-functionalized alkyl complexes of the general formula [Pd(PNP)(CHRCHR′Nu)](BF_4), which are unusually stable to β-H elimination.

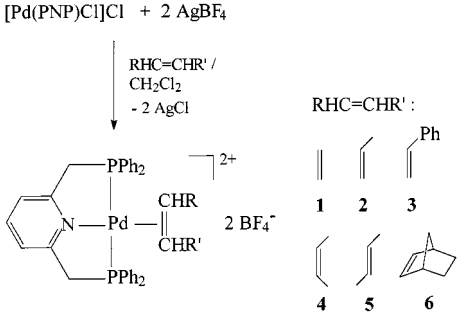
Introduction

(Olefin)palladium(II) complexes are important intermediates in organic syntheses and catalytic processes,[1] where the addition of nucleophiles to the C=C double bond is the crucial step. This offers numerous possibilities for the functionalization of simple olefins.[2] Among these, the hydroamination process, which was first investigated in the early 1970s, has recently attracted renewed attention.[3] The electrophilic character of the coordinated olefin is enhanced by an increase in the positive charge on the metal center,[4] as also shown by the ability of cationic Pd^{II} complexes to promote olefin polymerization[5] and copolymerization[6] reactions. Accordingly, very high reactivity would, in principle, be expected for complexes where the metal center bears a net (+2) charge, thus making such species appealing targets for investigation. On the other hand, a net (+2) charge would also enhance the electrophilic character and hardness of the metal center, and in such species the soft olefinic ligand can be expected to be readily displaceable, even by weak ligands and/or nucleophiles. Consequently, dicationic alkene complexes are expected to be accessible only within a rather narrow range of conditions and their reactivity is not readily predictable in advance. In line with the above considerations, no dicationic Pd^{II} complex of a simple monoolefin had been described in the literature[7] until we reported[8] the synthesis and characterization of two compounds of the formula [Pd(PNP)(CH_2=CHR)]$(BF_4)_2$ [PNP = 2,6-bis(diphenylphosphanylmethyl)-pyridine;[9] R = H, Ph], together with their reactions with secondary aliphatic amines. A number of questions arose from the above study, e.g. concerning the range of accessible (+2) charged complexes, their reactivity with nucleophiles weaker than aliphatic amines, and the nature (kinetic or thermodynamic) and extent of the competition between nucleophilic addition and displacement. In the present paper, we address these issues, presenting some quantitative evidence for the high electrophilicity of the olefin and for the interplay between addition and substitution reactions in these species. We also report the generation of a rare class of non-chelating β-functionalized (alkyl)Pd^{II} derivatives that are thermally stable and do not undergo β-H elimination.[10−13]

Results and Discussion

Synthesis and Characterization of [Pd(PNP)(olefin)]$^{2+}$ Complexes

The dicationic (olefin)palladium(II) complexes [Pd(PNP)(olefin)]$(BF_4)_2$ [olefin: CH_2=CH_2 (**1**), CH_2=CHMe (**2**), CH_2=CHPh (**3**), (*Z*)-MeCH=CHMe (**4**), (*E*)-



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MeCH=CHMe (**5**), norbornene (**6**)] were prepared by reaction of the chloro complex [Pd(PNP)Cl]Cl[14] with two equivalents of silver tetrafluoroborate in the presence of an excess of the olefin according to Equation (1). The preparation of complexes **1** and **3** by the same procedure has been described previously.[8] In an alternative synthetic route, the norbornene complex **6** could be prepared by displacement of ethylene with an excess of norbornene [Equation (2)] and was obtained in high yield in an analytically pure state.

$$\underset{\mathbf{1}}{[Pd(PNP)(CH_2{=}CH_2)](BF_4)_2} \xrightarrow[-\ CH_2{=}CH_2]{\text{norbornene/ } CH_2Cl_2} \underset{\mathbf{6}}{[Pd(PNP)(\text{norbornene})](BF_4)_2} \quad (2)$$

The complexes **2** and **4**−**6** were characterized by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy. They were found to be moderately stable in dichloromethane and nitromethane solution at room temperature and may be stored for months under a dry atmosphere. They slowly decompose in moist air, as was also observed for the ethylene and styrene complexes **1** and **3**.[8] The ^{1}H and ^{31}P NMR spectra of the complexes (see Experimental Section) indicate an averaged C_2 symmetry for the propene complex **2** and an averaged C_{2v} symmetry for the complexes **4** and **6** and hence a fast rotation of the olefin about the Pd−double bond axis in each case. The spectrum of the propene complex **2** does not show substantial changes on cooling down to 203 K, indicating that at this temperature olefin rotation is still fast on the NMR time scale. The pattern observed for the propene complex **2** also indicates that at room temperature the exchange (dissociation−reassociation) of the olefin is slow on the NMR time scale. This was confirmed for all the complexes examined by the appearance of well-separated signals for the protons of free and coordinated olefin when a small amount of free olefin was added to each sample.

The ^{13}C chemical shifts of the olefinic carbon atoms in the complexes **1**−**6** are listed in Table 1, together with the corresponding coordination-induced shifts Δδ. A rather uniform albeit modest upfield shift is observed: The average Δδ is −15 ppm for the methine carbon atoms (except in the case of norbornene) and −33 ppm for the methylene carbon atoms, confirming previous observations for complexes **1** and **3**.[8] As pointed out previously,[8] the small values of Δδ are consistent with the high positive charge present on the central ion (as compared with the isoelectronic Rh^{I} complexes[15]) and with a consequent presumably low contribution of π-back-donation to the metal−olefin bond.[16]

Table 1. ^{13}C NMR chemical shifts of the coordinated olefins in **1**−**6** ($\Delta\delta = \delta_{coord} - \delta_{free}$)

Olefin	δ(=CH_2)	Δδ(=CH_2)	δ(=CH)	Δδ(=CH)
$CH_2{=}CH_2$ [8]	88.0	−35.3		
MeCH=CH_2	86.4	−29.6	118.1	−16.5
PhCH=CH_2 [8]	77.2	−34.8	120.2	−15.3
(*Z*)-MeCH=CHMe			110.9	−14.4
(*E*)-MeCH=CHMe			107.8	−17.6
Norbornene			105.2	−30.5

Olefin Displacement

As mentioned in the previous section, in complexes **1**−**6** at room temperature the olefin exchange is slow on the NMR time scale, which seems to be a rather unusual feature for coordinatively unsaturated Pd^{II} complexes.[17] However, the exchange is fast on the laboratory time scale, as shown by an experiment in which free ethylene was added to an NMR sample of the propene complex **2** at room temperature. The ^{1}H NMR spectrum of the mixture, recorded within 3 min of mixing, showed the presence of both species **1** and **2**, the relative abundances of which remained unchanged with time, indicating a rapid equilibration of the olefin complexes. The equilibrium constant for the exchange [Equation (3)] of ethylene for propene was estimated as $K = 1.4$ by integration of the NMR signals of the four species involved. Similar experiments were performed on complexes **3**−**5**, allowing estimation of the respective equilibrium constants [Equation (3)].

$$\underset{\mathbf{2\text{-}5}}{[Pd(PNP)(\text{olefin})](BF_4)_2} + CH_2{=}CH_2 \quad \Big\Vert K\,(CD_2Cl_2) \quad (3)$$

olefin	*K*
propene	1.4
E-2-butene	3
Z-2-butene	6
styrene	26

$$\underset{\mathbf{1}}{[Pd(PNP)(CH_2{=}CH_2)](BF_4)_2} + \text{olefin}$$

The relative stabilities of the olefin complexes seem to be determined essentially by steric factors. It is worth noting that (*E*)-2-butene gives a more stable complex than (*Z*)-2-butene, in contrast to the sequence typically found for (2-butene)metal complexes.[16,18] This most likely arises from the C_2 symmetry of the "pocket" created by the PNP ligand, which is better suited for hosting the (*E*)- as compared to the (*Z*)-olefin. The substantially lower stability of the styrene complex **3** can be ascribed to a steric interaction between the phenyl groups, which was revealed by its X-ray structure.[8]

As anticipated in the introduction, the olefin in complexes **1**−**6** is easily displaced, even by ligands that are usually weakly coordinative towards d^8 ions. Dissolution in acetone led to loss of the olefin from all of the complexes, while saturation of dichloromethane solutions of **1**, **2**, or **3** with water followed by evaporation of the solvent furnished the aqua complex **7** [Equation (4)]. The displacement of ethylene by acetonitrile, giving complex **8**, proved to be even more favorable. In the latter two cases, the equilibrium constants for the exchange [Equation (4)] were determined by

^{1}H NMR measurements in CD_2Cl_2/CD_3NO_2 (4:1) and were found to be $K = 5{\cdot}10^{-2}$ and $K = 9{\cdot}10^{2}$ for **7** and **8**, respectively.

$$[Pd(PNP)(CH_2{=}CH_2)](BF_4)_2 + L \quad \mathbf{1}$$

L	K (CD_2Cl_2/CD_3NO_2)
H_2O	$5 \cdot 10^{-2}$
CH_3CN	$9 \cdot 10^{2}$

$$[Pd(PNP)(L)](BF_4)_2 + CH_2{=}CH_2 \qquad (4)$$

L = H_2O **7**; CH_3CN **8**

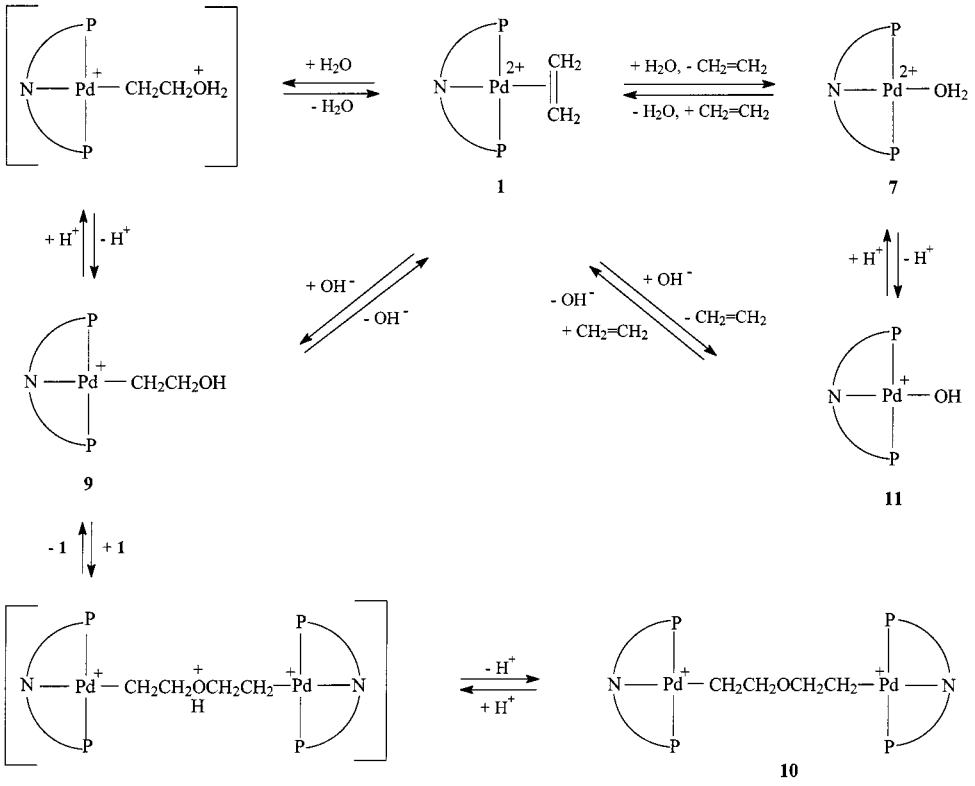
Reactions with Nucleophiles

Complexes **1**−**6** were treated with a number of nucleophiles, including water, methanol, and aliphatic and aromatic amines. In many cases, the reaction mixtures were directly analyzed by ^{1}H NMR, which revealed details that would have remained undetected in normal preparative experiments and hence provided a quantitative estimation of the factors controlling the behaviour of the system.

Reactions with H_2O

As mentioned above, treatment of the ethylene complex **1** with an excess of H_2O resulted in the displacement of the olefin with production of the aqua complex $[Pd(PNP)(H_2O)](BF_4)_2$ (**7**) [Equation (4)], which was isolated and characterized by ^{1}H NMR. However, when the reaction was performed in an NMR tube using an excess of ethylene and a drop of water (resulting in a biphasic mixture), signals appeared in the spectrum indicative of a partial conversion of **1** to addition products (see below). These addition products were almost undetectable in the absence of an excess of heterogeneous water. This qualitatively indicated the occurrence of an overall equilibrium, in which the nucleophilic attack on the coordinated olefin was followed by proton transfer to the water phase (see Scheme 1). Indeed, when the reaction was performed in the presence of solid $NaHCO_3$ (ca. 2 equiv.), the equilibrium was seen to be quantitatively shifted towards the addition products, which could be isolated as a solid mixture and were assigned the mono- and dialkylated structures **9** and **10** (Scheme 1). In the ^{1}H NMR spectrum of the mixture, two sets of signals are seen for the $[PdCH_2CH_2O]$ moiety at $\delta = 2.02$ and 3.44 for **9** and at $\delta = 1.79$ and 2.79 for **10**. Integration of these signals reveals a ratio of ca. 1:3. Correspondingly, two different signals are observed for the PCH_2 group of the coordinated PNP ligand, at $\delta = 4.38$ and $\delta = 4.44$, respectively, in the same 1:3 ratio. Reductive degradation of the product mixture with $NaBH_4$ in $[D_8]$THF gave a solution in which the ^{1}H NMR signals of ethanol and diethyl ether were found in the same 1:3 ratio as observed for **9** and **10** (corresponding to a molar ratio of 1:1.5), thus independently confirming the above assignments.

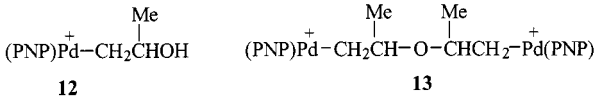
Both the substitution reaction and the nucleophilic attack were found to be readily reversible. Indeed, addition of 5 equiv. of concentrated HBF_4 to a sample of the alkyl derivatives **9** and **10** in the presence of free ethylene resulted in the formation of **1**. Also, treatment of the aqua complex



Scheme 1

7 with $NaHCO_3$ in dichloromethane saturated with ethylene likewise produced the same mixture of alkyl derivatives **9** and **10**. The formation of **10** was also performed in a stepwise manner, i.e. by first abstracting a proton from the coordinated water in **7** with an excess of $NaHCO_3$, giving the hydroxo complex $[Pd(PNP)(OH)]BF_4$ (**11**), and then treating the isolated complex **11** with ethylene. The latter reaction was monitored by ^1H NMR, which revealed the initial formation of the monoalkylated species **9** followed by partial conversion to **10**.

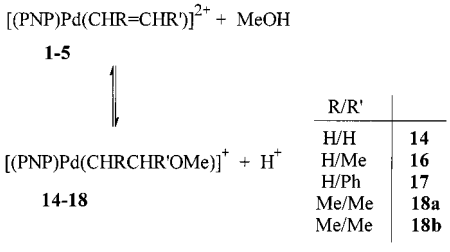
A similar set of equilibria were revealed in the case of the propene complex **2**. The major observed addition product (80% based on Pd) was the mononuclear primary alkyl derivative **12**, corresponding to a Markovnikov addition. Two pertinent differences from the ethylene case were qualitatively apparent. Firstly, the addition products were barely detectable in the absence of added $NaHCO_3$, indicating that the addition reaction is appreciably less favored than in the case of ethylene. Secondly, the binuclear species **13** was only produced as a minor product (20% based on Pd), probably reflecting the steric repulsion between two secondary carbon atoms linked to the same oxygen atom.



12 **13**

Reactions with MeOH

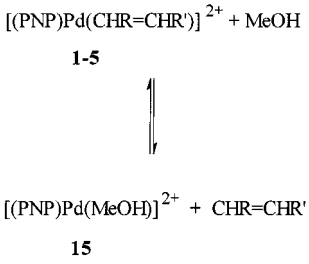
Dissolution of the ethylene complex **1** in CD_3OD produced a strongly acidic solution, the ^1H NMR spectrum of which revealed the presence of the addition product $[D_3]$**14**, a substitution product $[D_3]$**15**, and free ethylene in a molar ratio of 1:1:1. In the case of the propene complex **2**, the addition product $[D_3]$**16** was formed to a lesser extent (corresponding ratio 1:4:4), while for the styrene complex **3**, only the substitution product $[D_3]$**15** and free styrene were detectable in solution. Small amounts of the addition products were also detectable in the case of the 2-butene complexes **4** and **5**. Addition of an excess of free olefin to the solutions of **1** and **2** led to an increase in the relative amounts of the corresponding addition products **14** and **16**, respectively. These results indicate that in methanol solution two fast equilibrium reactions are operative [Equation (5) and Equation (6)].



R/R'	
H/H	**14**
H/Me	**16**
H/Ph	**17**
Me/Me	**18a**
Me/Me	**18b**

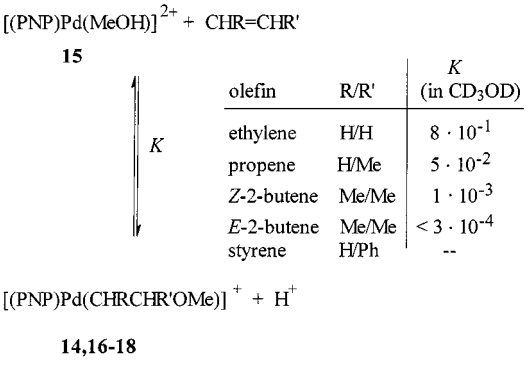
(5)

The equilibrium constants for the overall reaction [Equation (7)] were estimated for ethylene, propene, and the two



(6)

2-butenes, giving a relative measure of the stabilities of the (β-methoxyalkyl)palladium species compared with the respective free olefins.



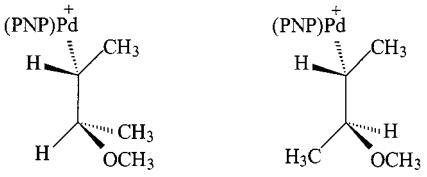
olefin	R/R'	K (in CD_3OD)
ethylene	H/H	$8 \cdot 10^{-1}$
propene	H/Me	$5 \cdot 10^{-2}$
Z-2-butene	Me/Me	$1 \cdot 10^{-3}$
E-2-butene	Me/Me	$< 3 \cdot 10^{-4}$
styrene	H/Ph	--

(7)

In the case of the ethylene complex **1**, the equilibrium represented by Equation (7) also results in a site exchange of the α- and β-protons of the alkyl chain. This exchange was actually revealed at room temperature by a ^1H NMR saturation transfer experiment, in which irradiation of either of the CH_2 groups caused a partial transfer of magnetization to the other CH_2 unit as well as to the free $CH_2=CH_2$ molecules, indicating that the overall exchange [Equation (7)] takes place at a rate comparable to the relaxation rates ($1-10\ s^{-1}$).

In line with our expectations, when the complexes **1**–**5** were treated with 2 equiv. of $NaHCO_3$ in methanol in the presence of an excess of free olefin, the equilibrium represented by Equation (7) was driven to completion leading to quantitative formation of the corresponding β-methoxyalkyl complexes **14** and **16**–**18**, which could be isolated. In the case of the ethylene complex **1**, the nucleophilic attack was also performed in a CH_2Cl_2 solution using 4 equiv. of MeOH, which led to the same result. High regioselectivity was achieved in the reactions of the propene and styrene complexes **2** and **3**, which gave **16** and **17**, respectively, in better than 97% abundances.[19] The structures of **16** and **17** were independently confirmed by reductive cleavage of the complexes with $NaBH_4$ in CD_3OD, which gave $CH_3CH(Me)OMe$ and $CH_3CH(Ph)OMe$, respectively. Addition of methanol to the (*Z*)- and (*E*)-2-butene complexes **4** and **5** furnished the diastereomers **18a** and **18b**, respectively, which could be distinguished by virtue of the slight but significant differences in their ^1H NMR spectra (see Experimental Section). The structures of **18a** and **18b** were

assigned assuming *trans* attack on the respective olefin complexes **4** and **5**. Although at present we are unable to provide any *direct* evidence for this assumption,[20] the alternative possibility of a *cis* addition (i.e. a true migratory insertion) seems unlikely in the light of previous knowledge on the stereochemistry of nucleophilic addition.[21] However, *circumstantial* evidence regarding this matter comes from the fact that although cationic (alkyl)(olefin) complexes of palladium(II) with bidentate ligands undergo rather fast insertion,[5] the isolated methyl derivative $[Pd(PNP)(CH_3)]BF_4$ is totally unreactive towards ethylene.[22]



18a **18b**

The obtained β-methoxyalkyl complexes are quite stable as solids and in solution, both when the σ-bonded carbon atom is primary (as in **14**, **16**, and **17**) and when it is secondary (as in **18a**,**b**). No interconversion between the two diastereomers **18a** and **18b** was observed in dichloromethane solution over a period of one week.

In spite of the commonly encountered high reactivity of norbornene, no addition product of methanol could be obtained from complex **6**, possibly because of steric instability of the σ-alkyl derivative that would be produced by the nucleophilic attack, or (as suggested by a referee) because of inertness of *exo*-η^2-norbornene towards *trans* addition.

In an attempt to cleave the Pd−C σ-bond protolytically, the β-methoxyalkyl complexes were treated with gaseous HCl in CD_2Cl_2 solution, allowing direct monitoring of the reaction by NMR. However, this led to an immediate reversion of the nucleophilic addition through heterolytic fragmentation. The respective olefin was liberated, along with MeOH and $[Pd(PNP)Cl]BF_4$.

$$\underset{\textbf{14, 16-18}}{[(PNP)Pd(CHRCHR'OMe)]BF_4} \xrightarrow{\substack{HCl\ (g)/\\ CD_2Cl_2}} [Pd(PNP)Cl]BF_4 + CHR{=}CHR' + MeOH \qquad (8)$$

For the complexes **18a** and **18b**, the reversion of the addition led almost exclusively to the formation of (*Z*)- and (*E*)-2-butene, respectively, which provides evidence for the microscopic reversibility of this reaction.

Reactions with Amines

The reactions of the secondary alkylamines piperidine and dimethylamine with the ethylene and styrene complexes **1** and **3** were recently reported from a purely preparative point of view.[8] We have now investigated the process in more detail and have extended the studies to less basic aromatic amines. After adding an excess of ethylene to a solution (0.007 mol L^{-1}) of the isolated dimethylamine complex **19**,[8] an equilibrium was attained within about 1 h at 283 K. The final solution contained the addition product **20**−H^+ together with very small but measurable amounts of the starting complex **19**. The ratio **20**−H^+/**19** was found to be proportional to the concentration of free ethylene, confirming the existence of the equilibrium and allowing estimation of the equilibrium constant for the formal "insertion"[23] reaction represented by Equation (9) ($K = 3 \cdot 10^4$ L mol^{-1}).

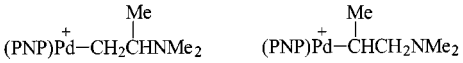
$$\underset{\textbf{19}}{[(PNP)Pd(Me_2NH)]^{2+}} + CH_2{=}CHR \quad \Big\Vert K_{ins}(CD_2Cl_2)$$

olefin	K_{ins} [L mol^{-1}]
ethylene	$3 \cdot 10^4$
propene	10^2

$$[(PNP)Pd(CH_2CHRNHMe_2)]^{2+} \qquad (9)$$

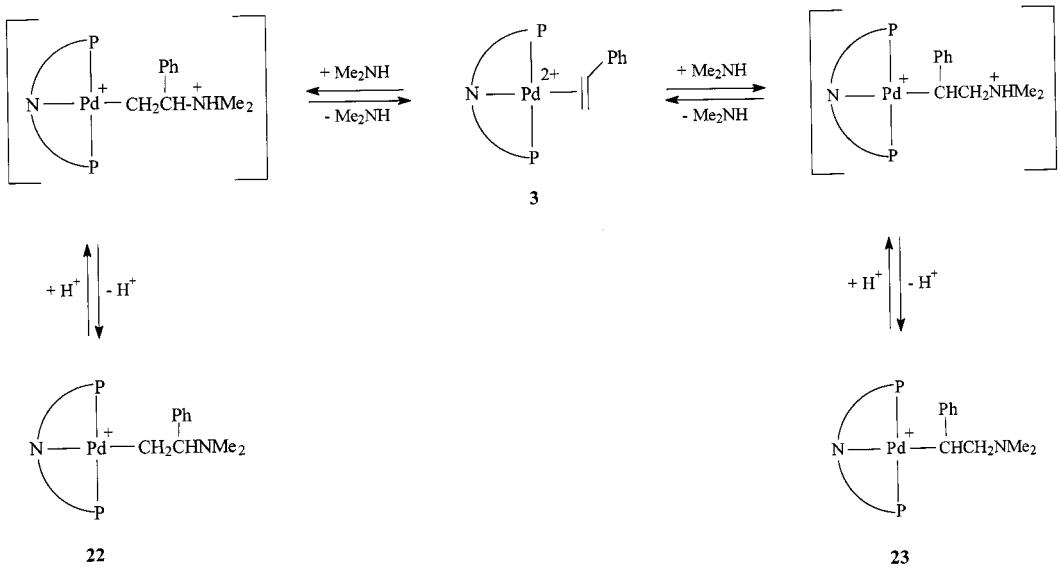
R = H, **20**-H^+,
R = Me, **21**-H^+

Similar experiments were performed using propene and styrene as the olefins. In the case of propene, the addition product **21**−H^+ was formed in an equilibrium reaction, the estimated constant for which was $K = 10^2$ L mol^{-1}. In the case of styrene, no addition product could be detected. However, when the reaction was performed starting from the styrene complex **3** and an excess (4 equiv.) of Me_2NH was added, the primary alkyl derivative **22** was formed immediately and completely isomerized within 1 h to the secondary (anti-Markovnikov) alkyl derivative **23** (Scheme 2). The same reaction with excess Me_2NH was also performed with the propene complex **2**, resulting in a mixture of **21** (82%) and the anti-Markovnikov product **24** (18%). The regiochemical assignments of the products **21**−**24** were confirmed by in situ reduction with sodium borohydride and ^1H NMR identification of the resulting amines. The higher stability of the secondary (anti-Markovnikov) alkyl derivative **23** compared to **22** is in contrast to the common trend shown by alkylmetal complexes (primary > secondary >> tertiary), but seems to reflect a common outcome in amination reactions of styrene.[3a]



21 **24**

Experiments similar to those described above were performed using aniline as a nucleophile. Starting from a solution (0.015 mol L^{-1}) of the isolated aniline complex **25** containing 0.1 mol L^{-1} of free ethylene, an equilibrium distribution of 10:1 between the starting complex and the addition product **26**−H^+ was attained within a few minutes. The estimated equilibrium constant for the formal "insertion"[23] reaction [Equation (10)] is $K = 1$ L mol^{-1}. Upon addition of $NaHCO_3$ (2 equiv.), the equilibrium was quantitatively driven towards the addition product **26**, which was



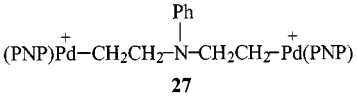
Scheme 2

formed together with small amounts of the dialkylated product **27**.[24]

$$[(PNP)Pd(PhNH_2)]^{2+} + CH_2{=}CH_2 \quad (\mathbf{25})$$

$$\Big\Vert \; K_{ins} = 1\ L\ mol^{-1}\ (CD_2Cl_2/CD_3NO_2) \qquad (10)$$

$$[(PNP)Pd(CH_2CH_2NH_2Ph)]^{2+} \quad (\mathbf{26}\text{-}H^+)$$



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In the above experiments, the equilibrium concentration of the ethylene complex **1** was below the limit of detection, hence the equilibrium constants for the substitution and addition reactions could not be directly evaluated. In order to estimate their individual values, the equilibrium constants of two auxiliary substitution reactions [Equation (11) and Equation (12)] were determined by ^{1}H NMR.

$$[(PNP)Pd(PhNH_2)]^{2+} + MeCN \quad (\mathbf{25})$$

$$\Big\Vert \; K = 4 \cdot 10^{-3}\ (CD_2Cl_2/CD_3NO_2) \qquad (11)$$

$$[(PNP)Pd(MeCN)]^{2+} + PhNH_2 \quad (\mathbf{8})$$

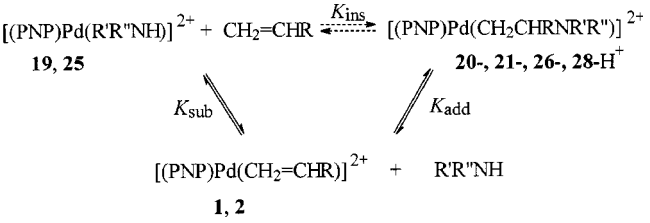
By combining these values with that for the ethylene displacement by acetonitrile [$K = 9{\cdot}10^2$, see Equation (4)], the equilibrium constants for the substitution (K_{sub}) and addition (K_{add}) reactions with aniline and dimethylamine were estimated. The values are reported in Table 2, together with the corresponding values for the propene complex **2**.

$$[(PNP)Pd(Me_2NH)]^{2+} + PhNH_2 \quad (\mathbf{19})$$

$$\Big\Vert \; K = 4 \cdot 10^{-4} \qquad (12)$$

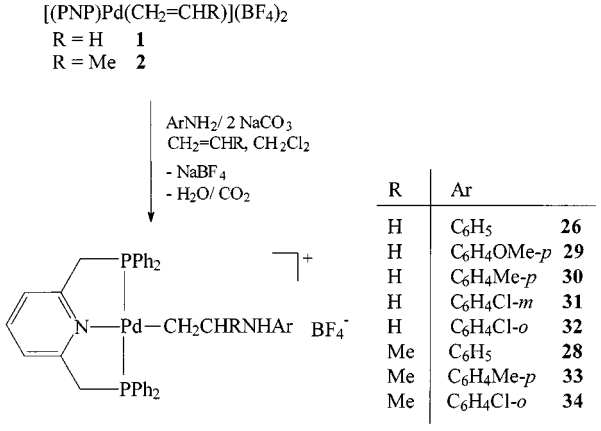
$$[(PNP)Pd(PhNH_2)]^{2+} + Me_2NH \quad (\mathbf{25})$$

Table 2. Approximate values of the equilibrium constants for the addition (K_{add}), substitution (K_{sub}), and "insertion" (see ref.[23]) ($K_{ins} = K_{add}/K_{sub}$) reactions of **1** and **2** with amines



((Scan 19)) Amine	Me_2NH			$PhNH_2$		
Olefin	K_{ins} [L·mol^{-1}]	K_{add} [L·mol^{-1}]	K_{sub}	K_{ins} [L·mol^{-1}]	K_{add} [L·mol^{-1}]	K_{sub}
$CH_2{=}CH_2$	$3{\cdot}10^4$	10^{13}	$6{\cdot}10^8$	1	$2{\cdot}10^5$	$2{\cdot}10^5$
$CH_2{=}CHMe$	$1{\cdot}10^2$	10^{11}	$1{\cdot}10^9$	$5{\cdot}10^{-2}$	$1.5{\cdot}10^4$	$3{\cdot}10^5$

The K_{add} values given in Table 2 show that nucleophilic attack on the coordinated olefin is a quite favorable process in the dicationic complex, even when the nucleophile is a poorly basic aromatic amine. Moreover, the acidic β-ammonioalkyl derivative generated in the reaction can be further converted into the more stable β-aminoalkyl species through proton abstraction by an auxiliary base. When the basicity of the amine decreases, the nucleophilic attack is less favored, but at the same time the β-ammonioalkyl derivative is more acidic, and a successive proton abstraction becomes more favored. Therefore, the overall reaction in the presence of an auxiliary base is expected to be driven to a similar extent towards the (β-aminoalkyl)palladium derivative. In view of these considerations, we treated complexes **1** and **2** with primary aromatic amines of varying basicity (ranging from 4-methoxyaniline, pK_a = 5.3 to 2-chloroaniline, pK_a = 2.6) and $NaHCO_3$ (2 equiv.) in the presence of an excess of the respective gaseous olefins. The (β-aminoethyl)Pd^{II} compounds **26** and **28−34** were indeed obtained in good yields (Scheme 3) as cream-colored solids and were characterized by ^1H NMR.



R	Ar	
H	C_6H_5	**26**
H	C_6H_4OMe-*p*	**29**
H	C_6H_4Me-*p*	**30**
H	C_6H_4Cl-*m*	**31**
H	C_6H_4Cl-*o*	**32**
Me	C_6H_5	**28**
Me	C_6H_4Me-*p*	**33**
Me	C_6H_4Cl-*o*	**34**

Scheme 3

The structures of the propene derivatives **28**, **33**, and **34** were assigned essentially as in the case of the water and methanol adducts, and indicated selective attack at the secondary carbon atom (Markovnikov addition). As in the case of the corresponding β-methoxyalkyl species **14** and **16−18**, the complexes **26** and **28−34** can be stored indefinitely as solids and are also stable in solution; no evidence for β-H elimination was observed after a week in dichloromethane. This stability towards β-H elimination is quite exceptional in (alkyl)Pd species that are not stabilized by four- or five-membered ring formation.[11] It most likely arises from the impossibility of the putative hydride ligand to access either of the *cis* positions, both of them being firmly bound by the two phosphane "arms" of the PNP ligand. It is noteworthy in this respect that the only β-functionalized open-chain alkyl Pd^{II} derivatives hitherto isolated are *trans*-$[Pd(PMe_3)_2(CH_2CH_2Y)Br]$ (Y = CO_2Me, CN).[13]

Conclusions

The use of the tridentate "pincer" ligand PNP has allowed the unprecedented isolation of stable dicationic (olefin)Pd^{II} complexes, and the subject of nucleophilic addition to Pd^{II}-coordinated olefins has been re-examined using these dicationic complexes as substrates. The σ-alkyl derivatives resulting from the nucleophilic attack are remarkably stable towards β-H elimination, as a consequence of the unavailability of the adjacent coordination sites. Since side-reactions arising from β-H elimination do not take place, for the first time approximate equilibrium data could be obtained for the nucleophilic addition and for the competitive substitution reaction. The results indicate that in a dicationic Pd^{II} complex the olefin is highly activated towards nucleophilic addition (much more so than in neutral species[25]), both kinetically and thermodynamically. It is relevant to note in this respect that in monocationic complexes containing a ligand isoelectronic and isostructural with PNP (i.e. PCP), no nucleophilic attack on a coordinated olefin is observed.[26] The coordinated double bond actually acts as a strong electrophile, as indicated by its ability to capture a lone pair from methanol and to successively protonate a base as weak as methanol itself. Viewed from another perspective, the σ-alkyl derivatives resulting from the nucleophilic attack are strongly stabilized by the residual positive charge on the metal ion, and it appears that the C−Pd σ-bond is *more* stabilized by the positive charge than the Pd−N bond of a coordinated amine. Thus, the formal "insertion"[23] of the olefin into the Pd−N bond is thermodynamically favored (Table 2), while it was found to be *disfavored* in the case of neutral species.[27] This finding could be relevant for the development of synthetically useful hydroaminations, because olefin displacement, which is considered to be a serious obstacle to achieving such processes,[3a] might become a minor concern or even be of no consequence in the case of dicationic species.

Experimental Section

General: All reactions were carried out under dry nitrogen. CH_2Cl_2 was refluxed with CaH_2, MeOH with $Mg/Mg(OMe)_2$, and diethyl ether with Na/benzophenone. The solvents were distilled prior to use. CD_2Cl_2, CD_3NO_3, and $CDCl_3$ were dried with 4-Å molecular sieves. $AgBF_4$ was obtained from ABCR and was used without further purification. The aromatic amines RNH_2 were obtained from Aldrich and were distilled prior to use. − NMR spectra were recorded with Varian Gemini 200, Bruker AC-200, Bruker AC-250, and Bruker WH-400 instruments. ^1H NMR shifts were referenced to the resonances of the residual protons in the solvents and the ^{13}C NMR shifts to the solvent resonances (δ = 53.8, CD_2Cl_2; δ = 62.8, CD_3NO_2). For the ^{31}P NMR spectra, H_3PO_4 (85%) was used as an external standard.

Syntheses: The complexes [Pd(PNP)Cl]Cl,[14] $[Pd(PNP)(CH_2=CHR)](BF_4)_2$ [R = H (**1**), Ph (**3**)], and $[Pd(PNP)(L)](BF_4)_2$ [L = MeCN (**8**), Me_2NH (**19**), pyridine (**35**)][8] were prepared according to previously described procedures.

[Pd(PNP)(olefin)](BF$_4$)$_2$ (2, 4−6). − General Procedure: A mixture of [Pd(PNP)Cl]Cl (200 mg, 0.306 mmol) and $AgBF_4$ (121 mg, 0.620 mmol) in CH_2Cl_2 (10 mL) was saturated with the appropriate gaseous olefin (in the case of norbornene 10 equiv. of the olefin was added). After stirring the mixture for 10 min, the precipitate was filtered off. In the case of 2-butenes and norbornene, the precipitate (containing the product) was washed with nitromethane (1 mL, free from any nitrile!). The product was precipitated from the solution by the dropwise addition of diethyl ether. The solid was collected by filtration, washed with diethyl ether, and dried in vacuo.

2: Yield 191 mg (0.243 mmol, 78%); ivory-colored solid; m.p. 181 °C (dec.). − $C_{34}H_{33}B_2F_8NP_2Pd$ (797.62): calcd. C 51.20, H 4.17, N 1.76; found C 50.91, H 4.21, N 1.69. − ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 1.51 (d, J_{HH} = 6.2 Hz, 3 H, CH_3), 4.56 (d pseudo t, J_{HH} = 17.2 Hz, N_{HP} = 5.4 Hz, 2 H, PCH_aH$_b$), 4.66 (d, J_{HH} = 14.8 Hz, 1 H, =CH_2), 4.70 (d, J_{HH} = 7.8 Hz, 1 H, =CH_2), 5.21 (d pseudo t, J_{HH} = 17.2 Hz, N_{HP} = 5.0 Hz, 2 H, PCH$_a$$H_b$), 6.00 (br, 1 H, =CH), 7.59−8.02 (m, 23 H, Ph, py). − ^{13}C NMR (50 MHz, CD_2Cl_2): δ = 21.5 (s, CH_3), 44.9 (pseudo t, N_{CP} = 12.8 Hz, PCH_2), 86.3 (s, =CH_2), 118.1 (s, =CH), 124.5 (pseudo t, N_{CP} = 25.5 Hz, Ph$_i$), 124.5 (br, py-3,5), 125.5 (pseudo t, N_{CP} = 27.3 Hz, Ph$_{i'}$), 131.2−131.3 (br, Ph$_m$), 133.8 (pseudo t, N_{CP} = 5.7 Hz, Ph$_o$), 134.9 (s, Ph$_p$), 135.1 (pseudo t, N_{CP} = 7.7 Hz, Ph$_{o'}$), 144.1 (s, py-4), 161.1 (br, py-2,6). − ^{31}P NMR (CH_2Cl_2, 81 MHz): δ = 46.9 (s).

4: Yield 196 mg (0.242 mmol, 79%); pale-yellow solid; m.p. 205 °C (dec.). − $C_{35}H_{35}B_2F_8NP_2Pd$ (811.64): calcd. C 51.79, H 4.35, N 1.73; found C 51.56, H 4.20, N 1.63. − ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 1.69 (br. d, J_{HH} = 3.6 Hz, 6 H, CH_3), 4.83 (pseudo t, N_{HP} = 5.2 Hz, 4 H, CH_2), 5.97 (br. q, 2 H, =CH), 7.50 (d, J_{HH} = 7.8 Hz, 2 H, py-3,5), 7.71 (m, 12 H, Ph), 7.83−8.03 (m, 9 H, py, Ph). − ^{13}C NMR (50 MHz, CD_2Cl_2): δ = 17.5 (s, CH_3), 44.2 (pseudo t, N_{CP} = 14.8 Hz, PCH_2), 110.8 (s, =CH), 124.8 (br, py-3,5), 131.2 (pseudo t, N_{CP} = 5.6 Hz, Ph$_m$), 134.7 (s, Ph$_p$), 134.9 (pseudo t, N_{CP} = 7.5 Hz, Ph$_o$), 144.2 (s, py-4), 160.4 (br, py-2,6). − ^{31}P NMR (CH_2Cl_2, 81 MHz): δ = 45.3 (s).

5: Yield 211 mg (0.260 mmol, 85%); pale-yellow solid. − $C_{35}H_{35}B_2F_8NP_2Pd$ (811.64): calcd. C 51.79, H 4.35, N 1.73; found C 51.50, H 4.16, N 1.60. − ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.47 (br. d, J_{HH} = 3.6 Hz, 6 H, CH_3), 4.76 (d pseudo t, N_{HP} = 5.6 Hz, J_{HH} = 17.4 Hz, 2 H, PCH_aH$_b$), 5.14 (d pseudo t, N_{HP} = 4.6 Hz, J_{HH} = 17.4 Hz, 2 H, PCH$_a$$H_b$), 5.86 (br. m, 2 H, =CH), 7.67−8.00 (m, 22 H, Ph, py), 8.11 (t, J_{HH} = 8.0 Hz, 1 H, py-4). − ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 19.1 (s, CH_3), 43.7 (pseudo t, N_{CP} = 14.1 Hz, PCH_2), 107.8 (s, =CH), 124.6 (pseudo t, N_{CP} = 5.3 Hz, py-3,5), 124.7 (pseudo t, N_{CP} = 27.1 Hz, Ph$_i$), 125.5 (pseudo t, N_{CP} = 26.1 Hz, Ph$_{i'}$), 130.5 (br, Ph$_m$), 133.1 (pseudo t, N_{CP} = 5.3 Hz, Ph$_o$), 134.3 (s, Ph$_p$), 134.3 (Ph$_{o'}$), 134.4 (s, Ph$_{p'}$), 144.2 (s, py-4), 160.3 (br, py-2,6). − ^{31}P NMR (CH_2Cl_2, 81 MHz): δ = 45.5 (s).

6. − Method A: According to the general procedure: yield 235 mg (0.251 mmol, 82%), ivory-colored solid. − **Method B:** To a solution of **1** (150 mg, 0.191 mmol) in CH_2Cl_2 (5 mL) was added ca. 10 equiv. of norbornene (2 mmol). After stirring the mixture for 1 h, the product was precipitated by the dropwise addition of diethyl ether. The solid was filtered off, washed three times with diethyl ether, and dried in vacuo. Yield 175 mg (0.187 mmol, 98%). − $C_{38}H_{37}B_2F_8NP_2Pd{\cdot}CH_2Cl_2$ (934.63): calcd. C 50.12, H 4.21, N 1.50; found C 49.80, H 4.03, N 1.39. − ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 0.77 (m, 1 H, norbornene), 1.34 (m, 1 H, norbornene), 1.55 (br, 4 H, norbornene), 1.94 (br, norbornene), 4.92 (t, J_{HP} = 4.2 Hz, 2 H, =CH, norbornene), 4.95 (pseudo t, N_{HP} = 5.0 Hz, 4 H, PCH_2), 7.57 (d, J_{HH} = 7.4 Hz, 2 H, py-3,5), 7.69−7.73 (m, 12 H, Ph), 7.86−7.98 (m, 9 H, Ph, py). − ^{13}C NMR (50 MHz, CD_3NO_2): δ = 23.6 (s, norbornene), 43.9 (s, norbornene), 46.0 (pseudo t, N_{CP} = 14.6 Hz), 54.5 (s, norbornene), 105.2 (s, =CH, norbornene), 124.6 (pseudo t, N_{CP} = 5.6 Hz, py-3,5), 125.4 (pseudo t, N_{CP} = 27.3 Hz, Ph$_i$), 130.7 (pseudo t, N_{CP} = 5.6 Hz, Ph$_m$), 134.1 (pseudo t, N_{CP} = 7.4 Hz, Ph$_o$), 134.7 (s, Ph$_p$), 144.2 (s, py-4), 159.9 (s, py-2,6). − ^{31}P NMR (81 MHz, CH_2Cl_2): δ = 50.4 (s).

[Pd(PNP)(H$_2$O)](BF$_4$)$_2$ (7): To a solution of **1** (100 mg, 0.127 mmol) in CH_2Cl_2 (6 mL) was added ca. 50 equiv. of H_2O (100 μL). After stirring for a few minutes, a yellow crystalline solid precipitated, which was collected by filtration, washed several times with diethyl ether, and dried in vacuo. Yield 90%. − ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 3.0 (v br, H_2O), 4.45 (br, 4 H, PCH_2), 7.54−8.05 (m, 23 H, Ph, py).

Reactions of 1 and 2 with H$_2$O: To a solution of **1** or **2** (100 mg) in CH_2Cl_2 (6 mL), saturated with ethylene or propene, respectively, 2 equiv. of $NaHCO_3$ and 50 equiv. of H_2O were added. The mixture was then stirred for 3 h, the solid was filtered off, and the solvent was removed under reduced pressure. A solid was obtained, which was recrystallized from CH_2Cl_2/diethyl ether.

9/10: Yield 87 mg (97% based on Pd); pale-yellow solid. − ^{1}H NMR (200 MHz, $CDCl_3$): **9**: δ = 2.02 (m, 2 H, $PdCH_2$), 3.44 (m, 2 H, CH_2), 4.44 (pseudo t, N_{HP} = 4.6 Hz, 4 H, PCH_2), 7.35−7.73 (m, 23 H, Ph, py). − **10**: δ = 1.79 (m, 2 H, $PdCH_2$), 2.78 (m, 2 H, CH_2), 4.38 (pseudo t, N_{HP} = 4.6 Hz, 4 H, PCH_2), 7.35−7.73 (m, 23 H, Ph, py). − ^{31}P NMR (81 MHz, CH_2Cl_2): **9/10**: δ = 24.1 (s).

12/13: Yield 82 mg (92% based on Pd); orange-yellow solid. − ^{1}H NMR (200 MHz, $CDCl_3$): **12**: δ = 0.81 (d, J_{HH} = 6.0 Hz, 3 H, CH_3), 2.01 (m, 2 H, $PdCH_2$), 3.66 (m, 1 H, CH), 4.44 (pseudo t, N_{HP} = 4.6 Hz, 4 H, PCH_2), 7.15−7.75 (m, 23 H, Ph, py). − **13**: δ = 1.17 (d, J_{HH} = 4 Hz, 3 H, CH_3), 2.01 (m, 2 H, $PdCH_2$), 3.65 (m, 1 H, CH), 4.44 (pseudo t, N_{HP} = 4.6 Hz, 4 H, PCH_2), 7.15−7.75 (m, 23 H, Ph, py). − ^{31}P NMR (81 MHz, CH_2Cl_2): **12/13**: δ = 22.3 (s), 23.7 (s).

Reductive Degradation with NaBH$_4$: To a suspension of 20 mg of the appropriate product mixture (**9/10** or **12/13**) in [D$_8$]THF (0.7 mL), cooled in an ice-bath, was added excess $NaBH_4$. After stirring for 1 h at room temperature, the dark-brown solution was filtered and the filtrate was analyzed by ^{1}H NMR spectroscopy.

[Pd(PNP)(OH)]BF$_4$ (11): A mixture of **7** (100 mg, 0.129 mmol) and 2 equiv. of $NaHCO_3$ in CH_2Cl_2 (5 mL) was stirred for 1.5 h. The mixture was then filtered and the product was precipitated from the filtrate by the dropwise addition of diethyl ether. The orange-yellow solid was collected by filtration, washed with diethyl ether, and dried in vacuo. Yield 85 mg (124 mmol, 96%). − ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 4.21 (pseudo t, N_{HP} = 4.4 Hz, 4 H, PCH_2), 7.15−7.75 (m, 23 H, Ph, py). − ^{31}P NMR (81 MHz, CH_2Cl_2): δ = 22.3 (s).

Reactions of [Pd(PNP)(CHRCHR′)](BF$_4$)$_2$ (1−5) with MeOH. − General Procedure: To a solution of **1−5** (100 mg) in MeOH (2 mL) cooled to 0 °C were added an excess of the appropriate olefin and 2 equiv. of $NaHCO_3$. The mixture was stirred for 3 h, the precipitate was filtered off, and the solvent was removed under reduced pressure. A beige solid was obtained in each case, which was recrystallized from CH_2Cl_2/diethyl ether.

[Pd(PNP)(CH$_2$CH$_2$OMe)]BF$_4$ (14): Yield 85%. − $C_{34}H_{34}BF_4NOP_2Pd$ (727.82): calcd. C 56.11, H 4.71, N 1.93; found

C 55.73, H 4.73, N 1.82. – ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 2.00 (m, 2 H, $PdCH_2$), 2.85 (s, 3 H, OCH_3), 3.10 (m, 2 H, CH_2), 4.43 (pseudo t, N_{HP} = 4.6 Hz, 4 H, PCH_2), 7.48–7.94 (m, 23 H, Ph, py). – ^{31}P NMR (81 MHz, CH_2Cl_2): δ = 24.4 (s).

[Pd(PNP){$CH_2CH(Me)OMe$}]BF_4 (16): Yield 86%. – $C_{35}H_{36}BF_4NOP_2Pd \cdot CH_2Cl_2$ (826.73): calcd. C 52.30, H 4.63, N 1.69; found C 51.26, H 4.46, N 1.62. – ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.68 (d, J_{HH} = 5.9 Hz, 3 H, CH_3), 1.67 (m, 1 H, $PdCH_2$), 2.20 (m, 1 H, $PdCH_2$), 2.74 (s, 3 H, OCH_3), 3.05 (m, 1 H, CH), 4.28–4.40 (m, 4 H, PCH_2), 7.50–7.68 (m, 22 H, Ph, py), 7.91 (t, J_{HH} = 7.8 Hz, 1 H, py-4).

[Pd(PNP){$CH_2CH(Ph)OMe$}]BF_4 (17): Yield 80%. – ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 2.00 (m, 1 H, PCH_2), 2.19 (m, 1 H, $PdCH_2$), 2.65 (s, 3 H, OCH_3), 3.78 (m, 1 H, CH), 4.41 (m, PCH_2), 6.84 (m, 2 H, CPh), 7.12 (m, 3 H, CPh), 7.49–7.95 (m, 23 H, PPh, py). – ^{31}P NMR (81 MHz, CH_2Cl_2): δ = 24.7 (s).

[Pd(PNP){CH(Me)CH(Me)OMe}]BF_4 [18a, obtained from (*Z*)-2-butene]: Yield 83%. – ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 0.82 (d, J_{HH} = 5.6 Hz, 3 H, CH_3), 0.92 (m, 3 H, CH_3), 2.74 (m, 2 H, CH–CH), 2.92 (s, 3 H, OCH_3), 4.31 (pseudo t, N_{HP} = 4.2 Hz, 4 H, PCH_2), 7.44–7.95 (m, 23 H, Ph, py). – ^{31}P NMR (81 MHz, CH_2Cl_2): δ = 21.8 (s).

[Pd(PNP){CH(Me)CH(Me)OMe}]BF_4 [18b, obtained from (*E*)-2-butene]: Yield 81%. – ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 0.93 (d, J_{HH} = 5.4 Hz, 3 H, CH_3), 1.04 (m, 3 H, CH_3), 2.72 (s, 3 H, OCH_3), 2.74 (m, 2 H, CH–CH), 4.35 (m, 4 H, PCH_2), 7.45–7.93 (m, 23 H, Ph, py).

Reductive Degradation of 16 and 17 with $NaBH_4$: To a solution of 20 mg of compound **16** or **17** in CD_3OD (0.7 mL), cooled in an ice-bath, was added excess $NaBH_4$. After stirring for 1 h at room temperature, the dark-brown solution was filtered and the filtrate was analyzed by ^{1}H NMR spectroscopy. – ^{1}H NMR: $CH_3CH(Me)OCD_3$: δ = 1.14 (d, J_{HH} = 6.2 Hz, 6 H, CH_3), 3.50 (sept, J_{HH} = 6.2 Hz, 1 H, CH).; $CH_3CH(Ph)OCD_3$: δ = 1.41 (d, J_{HH} = 6.1 Hz, 3 H, CH_3), 4.34 (q, J_{HH} = 6.1 Hz, 1 H, CH), 7.28 (m, 5 H, Ph).

Treatment of 14, 16–18a,b with HCl: Gaseous HCl was bubbled through solutions of **14**, **16–18a,b** in CD_2Cl_2, which led to a color change from orange to yellow. The ^{1}H NMR spectra of these solutions were found to feature signals attributable to both the free olefin and $[Pd(PNP)Cl]^+$.

[Pd(PNP)(MeOH)]$(BF_4)_2$ (15): Compound **1** (100 mg) was dissolved in MeOH (5 mL) and the solvent was removed under reduced pressure. This procedure was repeated twice more. Finally, the yellow solid was washed with diethyl ether and dried in vacuo. Yield 95%. – ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 3.17 (br, 1 H, OH), 3.38 (s, 3 H, CH_3), 4.49 (pseudo t, N_{HP} = 4.6 Hz, 4 H, PCH_2), 7.48–8.01 (m, 23 H, Ph, py).

Reactions of 19 with Ethylene and Propene: Solutions of **19** (3 mg) in CD_2Cl_2 (0.6 mL) were saturated with ethylene and propene, respectively.

[(PNP)$PdCH_2CH_2NHMe_2$]$^{2+}$ (20–H^+): NMR: δ = 1.82 (m, 2 H, $PdCH_2$), 2.28 (s, 6 H, NMe_2), 2.79 (m, 2 H, NCH_2), 4.52 (pseudo t, N_{HP} = 5.0 Hz, 4 H, PCH_2), 7.48–8.02 (m, 23 H, Ph, py).

[(PNP)$PdCH_2CH(Me)NHMe_2$]$^{2+}$ (21–H^+): NMR: δ = 0.82 (d, J_{HH} = 6.2 Hz, 3 H, CH_3), 1.79 (m, 1 H, $PdCH_2$), 1.92 (m, 1 H, $PdCH_2$), 2.15 (s, 3 H, NCH_3), 2.22 (s, 3 H, NCH_3), 2.89 (m, 1 H, CH), 4.56 (pseudo t, N_{HP} = 4.6 Hz, 4 H, PCH_2), 7.55–8.02 (m, 23 H, Ph, py).

Reaction of 3 with Me_2NH: Two NMR tubes were prepared, each containing a solution of **3** (8 mg) in CD_2Cl_2 (0.6 mL) with 4 equiv. of gaseous Me_2NH. A ^{1}H NMR spectrum was recorded immediately after the addition of the amine.

[(PNP)$PdCH_2CH(Ph)NMe_2$]$^+$ (22): NMR: δ = 1.68 [s, 6 H, $N(CH_3)_2$], 2.28 (m, 1 H, $PdCH_2$), 2.48 (m, 1 H, $PdCH_2$), 3.44 (m, 1 H, CH), 4.37 (pseudo t, 4 H, N_{HP} = 4.4 Hz, PCH_2), 6.55 (d, 2 H, J_{HH} = 8.2 Hz, Ph), 7.06 (m, 3 H, Ph), 7.53–7.98 (m, 23 H, PPh, py). – For the reductive degradation, an excess of $NaBH_4$ (dissolved in a drop of CD_3OD) was added instantly to one of the two solutions. After 20 min, its ^{1}H NMR spectrum was recorded again, which now featured signals due to $CH_3CH(Ph)NMe_2$. – The second sample was again analyzed by ^{1}H NMR after 1 h.

[(PNP)$PdCH(Ph)CH_2NMe_2$]$^+$ (23): NMR: δ = 1.89 [s, 6 H, $N(CH_3)_2$], 2.48 (m, 1 H, NCH_2), 2.68 (m, 1 H, PdCH), 3.98 (m, 1 H, NCH_2), 4.26 (d pseudo t, N_{HP} = 4.6 Hz, J_{HH} = 17 Hz, 2 H, PCH_aH_b), 4.40 (d pseudo t, N_{HP} = 4.4 Hz, J_{HH} = 17 Hz, 2 H, PCH_aH_b), 6.41 (d, J_{HH} = 7 Hz, 2 H, Ph), 6.87 (m, 3 H, Ph), 7.50–7.92 (m, 23 H, PPh, py). – After treatment of the solution with $NaBH_4$ (CD_3OD) as described above, the signals of $PhCH_2CH_2NMe_2$ were detectable.

Reaction of 2 with 4 Equiv. of Me_2NH: The reaction was carried out in an NMR tube in a similar manner as described for the reaction of **3** with Me_2NH.

[(PNP)$PdCH_2CH(Me)NMe_2$]$^+$ (21): ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 0.70 (d, J_{HH} = 6.2 Hz, 3 H, CH_3), 1.85 (m, 1 H, $PdCH_2$), 1.97 (s, 6 H, NCH_3), 2.05 (m, 1 H, $PdCH_2$), 2.62 (m, 1 H, CH), 4.48 (pseudo t, N_{HP} = 4.6 Hz, 4 H, PCH_2), 7.57–7.98 (m, 23 H, Ph, py).

[(PNP)$PdCH(Me)CH_2NMe_2$]$^+$ (24): ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 1.02 (d pseudo t, J_{HH} = 7.0 Hz, N_{HP} = 3 Hz, 3 H, CH_3), 1.84 (s, 6 H, NCH_3), 4.36 (pseudo t, N_{HP} = 4.4 Hz, 4 H, PCH_2), 7.55–8.02 (m, 23 H, Ph, py). The remaining signals for CH and CH_2 are overlapped with the signals due to **21**.

[Pd(PNP)($PhNH_2$)]$(BF_4)_2$ (25): To a solution of **1** (100 mg) in CH_2Cl_2 (3 mL) was added aniline (0.5 mL). After stirring for a few minutes, an ivory-colored solid crystallized, which was collected by filtration, washed three times with diethyl ether, and dried in vacuo. Yield 85%. – $C_{37}H_{34}B_2F_8N_2P_2Pd \cdot 0.75CH_2Cl_2$ (912.27): calcd. C 49.70, H 3.92, N 3.07; found C 49.79, H 3.91, N 3.14. – ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 4.59 (pseudo t, N_{HP} = 4.8 Hz, 4 H, PCH_2), 5.70 (br, 2 H, NH_2), 6.67 (d, J_{HH} = 7.6 Hz, 2 H, NPh), 6.89 (m, 3 H, NPh), 7.55–7.80 (m, 22 H, Ph, py), 7.88 (t, J_{HH} = 7.6 Hz, 1 H, py-4).

Reactions of 25 with Ethylene and Propene: A solution of **24** (8 mg) in CD_2Cl_2/CD_3NO_2 (6:1) (0.6 mL) was saturated with either ethylene or propene. Since the signals of the addition products appear in the spectra at relatively low intensity and are partly overlapped by the signals of **25**, the full set of signals could not be detected.

[(PNP)$PdCH_2CH_2NH_2Ph$]$^{2+}$ (25–H^+): NMR: δ = 2.12 (m, 1 H, $PdCH_2$), 3.28 (m, 1 H, NCH_2), 4.47 (pseudo t, N_{HP} = 4.8 Hz, 4 H, PCH_2).

[(PNP)$PdCH_2CH(Me)NH_2Ph$]$^{2+}$ (26–H^+): NMR: δ = 0.92 (d, J_{HH} = 6.0 Hz, 3 H, CH_3).

Preparation of [Pd(PNP)($CH_2CHRNHAr$)]$(BF_4)_2$ (26, 28–34) – General Procedure: A solution of **1** or **2** (100 mg) in CH_2Cl_2 (2 mL) was cooled to 0 °C and saturated with the appropriate olefin; 2

equiv. of $NaHCO_3$ and 4 equiv. of $ArNH_2$ were then added. After stirring the mixture for 3 h, the precipitate was filtered off and the filtrate was concentrated to dryness under reduced pressure. A beige solid was obtained, which was recrystallized from CH_2Cl_2/diethyl ether.

[Pd(PNP)(CH_2CH_2NHPh)]BF_4 (26): Yield 87%. – $C_{39}H_{37}BF_4N_2P_2Pd{\cdot}0.5CH_2Cl_2$ (831.31): calcd. C 57.07, H 4.60, N 3.37; found C 56.72, H 4.58, N 3.26. – ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 2.09 (m, 2 H, $PdCH_2$), 2.93 (br, 2 H, CH_2N), 3.41 (br, 1 H, NHPh), 4.43 (pseudo t, N_{HP} = 4.6 Hz, 4 H, PCH_2), 5.98 (d, J_{HH} = 7.6 Hz, 2 H, NPh_o), 6.54 (t, J_{HH} = 7.4 Hz, 1 H, NPh_p), 6.92 (t, J_{HH} = 7.4 Hz, 2 H, NPh_m), 7.53–7.88 (m, 22 H, Ph, py), 7.94 (t, J_{HH} = 7.2 Hz, 1 H, py-4). – ^{31}P NMR (81 MHz, CH_2Cl_2): δ = 23.8 (s).

[Pd(PNP)($CH_2CH_2NHC_6H_4OMe$-*p*)]BF_4 (29): Yield 80%. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.05 (m, 2 H, $PdCH_2$), 2.86 (br, 2 H, NCH_2), 3.07 (br, 1 H, NH), 3.68 (s, 3 H, CH_3) 4.45 (pseudo t, N_{HP} = 4.8 Hz, 4 H, PCH_2), 5.95 (d, J_{HH} = 9.2 Hz, 2 H, NC_6H_4), 6.54 (d, J_{HH} = 9.2 Hz, 2 H, NC_6H_4), 7.50–7.82 (m, 23 H, Ph, py). – ^{31}P NMR (81 MHz, CH_2Cl_2): δ = 23.6 (s).

[Pd(PNP)($CH_2CH_2NHC_6H_4Me$-*p*)]BF_4 (30): Yield 84%. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.05 (m, 2 H, $PdCH_2$), 2.15 (s, 3 H, CH_3), 2.89 (br, 2 H, NCH_2), 3.19 (br, 1 H, NH), 4.44 (pseudo t, N_{HP} = 4.6 Hz, 4 H, PCH_2), 5.80 (d, J_{HH} = 8.2 Hz, 2 H, NC_6H_4), 6.73 (d, J_{HH} = 8.2 Hz, 2 H, NC_6H_4), 7.49–7.74 (m, 23 H, Ph, py). – ^{31}P NMR (81 MHz, CH_2Cl_2): δ = 23.6 (s).

[Pd(PNP)($CH_2CH_2NHC_6H_4Cl$-*m*)]BF_4 (31): Yield 81%. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.03 (m, 2 H, $PdCH_2$), 2.79 (br, 2 H, CH_2N), 3.50 (br, 1 H, NH), 4.45 (pseudo t, N_{HP} = 4.2 Hz, 4 H, PCH_2), 5.88 (m, 2 H, NC_6H_4Cl), 6.48 (d, J_{HH} = 8.2 Hz, 1 H, NC_6H_4Cl), 6.81 (t, J_{HH} = 8.4 Hz, 1 H, NC_6H_4Cl), 7.52–7.72 (m, 23 H, Ph, py). – ^{31}P NMR (81 MHz, CH_2Cl_2): δ = 23.6 (s).

[Pd(PNP)($CH_2CH_2NHC_6H_4Cl$-*o*)]BF_4 (32): Yield 81%. – $C_{39}H_{36}BF_4N_2P_2Pd \cdot 1.5\,CH_2Cl_2$ (950.68): calcd. C 51.11, H 4.13, N 2.94; found C 50.76, H 4.01, N 2.86. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.09 (m, 2 H, $PdCH_2$), 2.94 (br, 2 H, CH_2N), 4.03 (br t, J_{HH} = 5.0 Hz, 1 H, NH), 4.46 (pseudo t, N_{HP} = 4.8 Hz, 4 H, PCH_2), 5.78 (d, J_{HH} = 8.0 Hz, 1 H, NC_6H_4Cl), 6.48 (d, J_{HH} = 7.8 Hz, 1 H, NC_6H_4Cl), 6.78 (t, J_{HH} = 8.0 Hz, 1 H, NC_6H_4Cl), 7.11 (d, J_{HH} = 7.8 Hz, 1 H, NC_6H_4Cl), 7.46–7.83 (m, 23 H, Ph, py).

[Pd(PNP){$CH_2CH(Me)NHPh$}]BF_4 (28): Yield 83%. – ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 0.84 (d, J_{HH} = 6.3 Hz, 3 H, CH_3), 1.94 (m, 1 H, CH_2), 2.20 (m, 1 H, CH_2), 3.12 (d, J_{HH} = 9.1 Hz, 1 H, NH), 3.27 (m, 1 H, CH), 4.39 (pseudo t, N_{HP} = 4.7 Hz, 4 H, PCH_2), 5.87 (d, J_{HH} = 7.8 Hz, 2 H, NPh), 6.53 (t, J_{HH} = 7.5 Hz, 1 H, NPh), 6.87 (t, J_{HH} = 7.8 Hz, 2 H, NPh), 7.48–7.75 (m, 22 H, PPh, py-3,5), 7.95 (t, 1 H, py-4).

[Pd(PNP){$CH_2CH(Me)NHC_6H_4Me$-*p*}]BF_4 (33): Yield 86%. – ^{1}H NMR (200 MHz, CD_2Cl_3): δ = 0.83 (d, J_{HH} = 7.0 Hz, 3 H, CH_3), 1.92 (m, 1 H, CH_2), 2.15 (s, 3 H, CH_3) 2.20 (m, 1 H, CH_2), 2.96 (d, J_{HH} = 9.0 Hz, 1 H, NH), 3.24 (m, 1 H, CH), 4.38 (pseudo-t, N_{HP} = 4.5 Hz, 4 H, PCH_2), 5.82 (d, J_{HH} = 7.1 Hz, 2 H, NC_6H_4), 6.71 (d, J_{HH} = 7.1 Hz, 2 H, NC_6H_4), 7.50–7.95 (m, 23 H, PPh, py).

[Pd(PNP)($CH_2CH(Me)NHC_6H_4Cl$-*o*)]BF_4 (34): Yield 81%. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.85 (d, J_{HH} = 6.2 Hz, 3 H, CH_3), 1.89 (m, 1 H, CH_2), 2.21 (m, 1 H, CH_2), 3.27 (m, 1 H, CH), 3.93 (d, J_{HH} = 9.0 Hz, 1 H, NH), 4.46 (pseudo t, N_{HP} = 4.6 Hz, 4 H, PCH_2), 5.74 (d, J_{HH} = 7.4 Hz, 1 H, NC_6H_4Cl), 6.46 (t, J_{HH} = 7.0 Hz, 1 H, NC_6H_4Cl), 6.73 (t, J_{HH} = 7.8 Hz, 1 H, NC_6H_4Cl), 7.09 (d, J_{HH} = 8 Hz, 1 H, NC_6H_4Cl), 7.44–7.85 (m, 23 H, PPh, py).

Reaction of 26 with 1: To a solution of **26** (7 mg) in CD_2Cl_2 (0.6 mL) saturated with ethylene, **1** (8 mg) was added, which led to a color change to reddish. An excess of $NaHCO_3$ was added and the mixture was stirred overnight, after which it had become yellow.

27: ^{1}H NMR (200 MHz): δ = 1.74 (m, 4 H, $PdCH_2$), 2.78 (t br, J = 7.8 Hz, 4 H, CH_2N), 4.35 (pseudo-t, N_{HP} = 4.8 Hz, 8 H, PCH_2), 5.73 (d, J_{HH} = 8.0 Hz, 2 H, NPh_o), 6.33 (t, J_{HH} = 7.2 Hz, 1 H, NPh_p), 6.62 (t, J_{HH} = 7.2 Hz, 1 H, NPh_m), 7.41–7.96 (m, 46 H, Ph, py).

Equilibrium Constant Determinations: The equilibrium constants for the exchange and addition reactions were determined by ^{1}H NMR analysis of equilibrium mixtures at 298 K (methanol addition reactions) or 283 K (all other cases) in CD_2Cl_2 or CD_2Cl_2/CD_3NO_2 (4:1) solution (c = 7–15 mM). With one exception (addition of Me_2NH to propene complex **2**), the reported values are the average result of three measurements run at different olefin or ligand concentrations. Very unbalanced exchange equilibria [e.g. Equation (11)] were handled by treating a solution of the most stable complex with a large excess of the exchanging ligand. The amine addition equilibria (olefin "insertion"[23]) were handled by treating a solution of the pure [Pd(PNP)(amine)]$(BF_4)_2$ complex (**19** or **25**) with an excess of the olefin. In this approach, the amount of free amine in the solution was made negligible and hence the simultaneous occurrence of proton-transfer equilibria to the free base could also be neglected. For the ligand-exchange reactions solutions (0.015 M) of **2**–**5** [Equation (3)], **1** [Equation (4), L = H_2O], and **25** [Equation (11)] were prepared and treated with an excess of the appropriate substituting ligand. In the case of the ethylene/MeCN exchange [Equation (4)], a solution of **8** was treated with a large excess of ethylene. The equilibrium constant for the $PhNH_2/Me_2NH$ exchange [Equation (12)] could not be determined directly because of an overlapping of all the relevant signals of the four species. Therefore, the constants of two further auxiliary equilibria were measured, involving the exchanges pyridine/Me_2NH (K = 1 in CD_2Cl_2) and $PhNH_2$/pyridine ($K = 4{\cdot}10^{-4}$ in CD_2Cl_2/CD_3NO_2).

Acknowledgments

We thank the Deutsche Akademie der Naturforscher Leopoldina (BMBF-LPD 9801-4) (C. H.) and the MURST (PRIN 9803243241) for financial support. We also thank the CIMCF, Università di Napoli "Federico II" for providing access to NMR facilities. We are grateful to Prof. D. Steinborn for helpful discussions.

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[19] The ^1H NMR spectrum of **16** shows three multiplets (1 H each) at δ = 3.05, 2.20, and 1.67, and a doublet (3 H) at δ = 0.68, which can be assigned to the $-CH_2CH(Me)-$ fragment, the most downfield signal being attributable to a −CH−O fragment. In a homodecoupling experiment, irradiation of the signal at δ = 3.05 led to decoupling of the methyl doublet at δ = 0.68, thus unambiguously assigning the former to the C*H*Me proton and thereby pointing to a structure corresponding to a Markovnikov addition (**16**). In the ^1H NMR spectrum of **17**, two multiplets at δ = 2.00 and 2.19 are seen for the $Pd-CH_2$ moiety, while a multiplet at δ = 3.78 (1 H) can be assigned to the C*H*Ph fragment to which the methoxy group is bound.

[20] The best way of establishing the stereochemistry of the addition would be an X-ray structure determination of either **18a** or **18b**, but as yet we have been unable to obtain suitable crystals of the complexes. The methine H−H coupling constants (7.1 and 9.1 Hz, respectively, in CD_3OD) could also be useful for this purpose, but only in conjunction with a detailed theoretical study aimed at establishing the conformational distribution of the species. To be reliable, such a QM/MM investigation should take in account the interactions with the solvent and the counterion, which is beyond the scope of the present paper and might be worthy of a separate study.

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[23] The term "insertion" refers only to the formal outcome of the reaction and does not have any mechanistic implication. It is likely that the actual mechanism involves a (bimolecular) substitution of the amine ligand followed by external *trans* nucleophilic attack on the coordinated olefin.

[24] To confirm the assigned structure, the dinuclear complex **27** was independently prepared by the reaction of **1** with **26** in the presence of 2 equivs. of $NaHCO_3$; see Experimental Section.

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Received June 23, 2000
[I00251]