Organometallics **1998,** *17,* 2060−2066

Coordination of Olefins and N-Donor Ligands at the Fragment [2,6-Bis((diphenylphosphino)methyl)pyridine]-palladium(II). Synthesis, Structure, and Amination of the New Dicationic Complexes $[Pd(PNP)(CH_2{=}CHR)](BF_4)_2$ (R = H, Ph)

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Received August 11, 1997

Dicationic complexes of palladium(II) containing the tridentate ligand 2,6-bis((diphenylphosphino)methyl)pyridine (PNP) of the general formula $[Pd(PNP)L](BF_4)_2$ (L = MeCN, pyridine, C_2H_4, $CH_2{=}CHPh$) have been prepared from $Pd(PNP)Cl_2$ by addition of 2 equiv of $AgBF_4$ in the presence of an excess of the respective ligand L in CH_2Cl_2. The corresponding amine complex (L = $NHMe_2$) was obtained by substitution of the acetonitrile from $[Pd(PNP)(MeCN)](BF_4)_2$ by $NHMe_2$ at 0 °C. The complexes were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, and the molecular structure of the styrene complex was determined by X-ray diffraction analysis. The spectral and structural parameters of the complexes are discussed in comparison to those of the recently prepared Rh(I) analogues. Nucleophilic attack of secondary amines on the coordinated olefins gave the corresponding β-aminoethyl complexes from which, upon reductive degradation, the respective ethylamines were obtained, showing selective anti-Markovnikov addition in the case of the styrene complex.

Introduction

The only reported catalytic addition of secondary amines to a simple olefin under mild conditions was obtained, although with a low turnover, with the cationic rhodium(I) ethylene complex $[Rh(C_2H_4)(PPh_3)_2(Me_2CO)]PF_6$.[1]

To study the mechanism of this reaction in detail, the structure and reactivity of model complexes containing the [2,6-bis((diphenylphosphino)methyl)pyridine]rhodium(I) fragment $[Rh(PNP)]^+$ as a stable structural unit were investigated.[2,3] Although the nucleophilic attack of the amine on the π-coordinated olefin is reputably the crucial step in the rhodium-catalyzed hydroamination reaction,[4] this failed in the case of the $[Rh(PNP)(olefin)]^+$ model complexes, which reacted by substitution of the coordinated olefin, giving the corresponding amine complexes.[2]

On the other hand, it is well-known that the stoichiometric olefin amination can be carried out by nucleophilic attack of an amine on palladium(II)[5] and platinum(II)[6] complexes. It seemed therefore interesting for the model studies to compare the structure and reactivity of related complexes in which the complete ligand sphere is maintained and only the metal ion is changed from rhodium(I) to palladium(II). In this way direct evidence may be obtained about the influence of the central ion on the structural parameters and on the electrophilic character of the coordinated olefin. We report in this paper the synthesis and characterization of the dicationic palladium(II) N-donor ligand complexes $[Pd(PNP)L](BF_4)_2$ (L = MeCN, pyridine, $NHMe_2$). We also report the synthesis of the complexes $[Pd(PNP)(CH_2{=}CHR)](BF_4)_2$ (R = H, Ph), which appear to be the first dicationic monoolefin Pd(II) complexes to be isolated, and the crystal structure of the styrene complex, as well as their reactivity toward secondary amines.

Results and Discussion

Synthesis and Characterization of Dicationic Palladium(II) N-Donor Ligand Complexes. To

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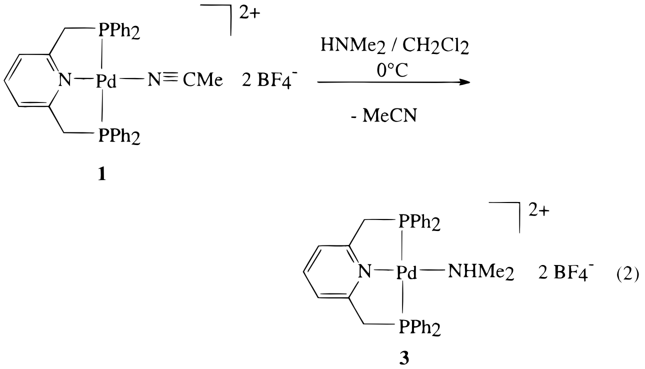
S0276-7333(97)00699-7 CCC: $15.00

investigate an appropriate synthetic route for dicationic PNP–palladium(II) complexes as well as their general properties, first complexes with different N-donor ligands (N(sp) → N(sp^2) → N(sp^3)) were prepared. The synthesis of the acetonitrile complex $[\mathrm{Pd(PNP)(MeCN)}](\mathrm{BF_4})_2$ was already described by DuBois and co-workers,[7] where, however, a mixture of the acetonitrile complex and the dinuclear complex $[\mathrm{Pd_2(PNP)_3}](\mathrm{BF_4})_4$ was obtained by the reaction of the PNP ligand with $[\mathrm{Pd(MeCN)_4}](\mathrm{BF_4})_2$ in acetonitrile. In our case the pure acetonitrile and pyridine complexes $[\mathrm{Pd(PNP)L}](\mathrm{BF_4})_2$ (L = MeCN (**1**), pyridine (**2**)) could be synthesized from $\mathrm{Pd(PNP)Cl_2}$[8] with 2 equiv of $\mathrm{AgBF_4}$ and an excess of the ligand L in dichloromethane at room temperature according to eq 1.

$$\mathrm{Pd(PNP)Cl_2} + 2\mathrm{AgBF_4} \xrightarrow{\mathrm{L/CH_2Cl_2}} [\mathrm{Pd(PNP)L}](\mathrm{BF_4})_2 + 2\mathrm{AgCl} \quad (1)$$

1, L = $\mathrm{CH_3CN}$
2, L = pyridine

Complexes **1** and **2** were obtained in good yields as crystalline solids which are soluble in dichloromethane, chloroform, acetone, acetonitrile, and methanol and insoluble in diethyl ether and hydrocarbons such as toluene and hexane. In the solid state, the acetonitrile complex **1** decomposes in moist air while the pyridine complex **2** is moderately stable. The corresponding amine complex $[\mathrm{Pd(PNP)(NHMe_2)}](\mathrm{BF_4})_2$ (**3**) could not be prepared from $\mathrm{Pd(PNP)Cl_2}$ and silver salt in the presence of $\mathrm{NHMe_2}$ in $\mathrm{CH_2Cl_2}$ or acetone, since decomposition occurred at room temperature as well as at 0 °C. However, the amine complex could be obtained via displacement of the acetonitrile ligand from $[\mathrm{Pd(PNP)(MeCN)}](\mathrm{BF_4})_2$ by dimethylamine at 0 °C (cf. eq 2).



1

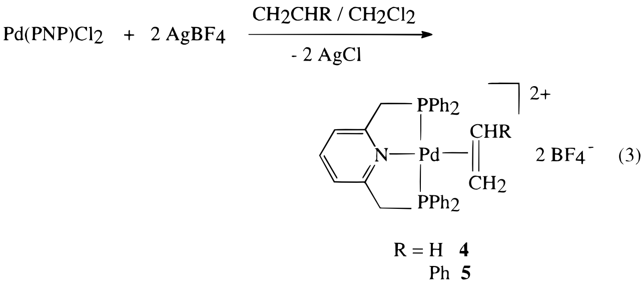
3

The amine complex **3**, which precipitated as a beige crystalline solid upon dropping diethyl ether into the concentrated reaction solution, is less stable than the acetonitrile complex **1**. Even at room temperature complex **3** releases dimethylamine and changes color to brown. The dissolution of the complex **3** in chloroform, dichloromethane, acetone, or methanol is accompanied by precipitation of a dark oil.

In the IR spectrum of complex **1** the two characteristic bands at 2305 and 2340 $\mathrm{cm^{-1}}$ indicate the coordinated acetonitrile.[9] The coordination of the PNP ligand in complexes **1**–**3** is suggested by the two bands[10] at about 1568 and 1603 $\mathrm{cm^{-1}}$ and the noncoordination of the $\mathrm{BF_4^-}$ anions by the strong band at 1058 $\mathrm{cm^{-1}}$.[11]

The N-donor ligand complexes were further characterized by ^{31}P and ^{1}H NMR spectroscopy. The ^{13}C NMR spectra are also available, except for the amine complex **3**, due to its relatively fast decomposition in solution. When the NMR data are compared to those of the corresponding Rh(I) complexes,[2,3] relevant systematic differences are found only for the ^{31}P resonances and for the proton resonances of the methylene groups bound to phosphorus, while the other signals are not significantly displaced. In the ^{31}P NMR spectrum a singlet appears at δ 36.1 for **1** (in $\mathrm{CD_2Cl_2}$), at δ 38.3 for **2** (in acetone-d_6), and at δ 37.3 for **3** (acetone-d_6). The signals are shifted downfield compared to those of the analogous rhodium(I) complexes $[\mathrm{Rh(PNP)L}]\mathrm{BF_4}$, whose signals are at δ 31.7 (L = MeCN), δ 30.9 (L = pyridine), and δ 34.3 (L = $\mathrm{NHMe_2}$), respectively, in acetone-d_6..[2,3] Also, a rather downfield shift of the virtual triplet of the methylene protons of the PNP ligand is observed which appears in the ^{1}H NMR spectra at δ 4.66 (in $\mathrm{CD_2Cl_2}$, **1**), δ 5.14 (in acetone-d_6, **2**), and δ 4.68 (in $\mathrm{CDCl_3}$, **3**) in comparison to those for the respective rhodium(I) analogues at δ 4.29 (L = MeCN), δ 4.36 (L = pyridine), and δ 4.22 (L = $\mathrm{NHMe_2}$) in acetone-d_6.[2,3] The observed trend reflects the greater positive charge of the $\mathrm{Pd^{2+}}$ compared to the $\mathrm{Rh^{+}}$ cation, whose effect on chemical shifts is reasonably expected to be greater on directly bonded ligand atoms, especially when they have a soft character, as do the phosphine P atoms and the π-bonded C=C double bond.

Synthesis and Structure of Dicationic Palladium(II) Olefin Complexes. The dicationic palladium(II) olefin complexes $[\mathrm{Pd(PNP)(CH_2{=}CHR)}](\mathrm{BF_4})_2$ (R = H (**4**), Ph (**5**)) could be obtained in good yields in the same manner as described for the complexes **1** and **2** from $\mathrm{Pd(PNP)Cl_2}$ and 2 equiv of silver tetrafluoroborate in the presence of an excess of the free olefin, according to eq 3.



The ethylene complex **4** precipitated as an ivory-colored crystalline solid by dropping diethyl ether into the solution. The yellow styrene complex **5** crystallized upon concentration of the solution. Both olefin complexes decompose in moist air as solids and are moderately stable in solution only in the presence of an excess of the corresponding free olefin. To the best of our knowledge, these are the first dicationic palladium(II) monoolefin complexes that have been isolated. To

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Table 1. ^{13}C and ^{1}H NMR Chemical Shifts (δ) of the Free and Coordinated Olefins in $[Pd(PNP)(olefin)](BF_4)_2$ and $[Rh(PNP)(olefin)]BF_4$[2]

compd	C(1)	C(2)	H(1z)	H(1e)	H(2)
$CH_2{=}CH_2$	123.3			5.30	
$[Pd(PNP)(CH_2{=}CH_2)]^{2+}$ [a]	88.0			4.49	
$[Rh(PNP)(CH_2{=}CH_2)]^{+}$ [b]	59.5			3.54	
$PhCH{=}CH_2$	112.0	135.5	5.24	5.74	6.72
$[Pd(PNP)(PhCH{=}CH_2)]^{2+}$ [a]	77.2	120.2	4.46	5.16	6.56
$[Rh(PNP)(PhCH{=}CH_2)]^{+}$ [b]	51.5	75.8	3.72	3.87	4.96

[a] In CD_2Cl_2. [b] In acetone-d_6.

avoid displacement and/or nucleophilic attack on the coordinated olefin, it proved important to perform the reaction in the absence of other potential donors, and the anhydrous silver salt was thus added as a solid, which could dissolve in CH_2Cl_2 because of transient complexation by the excess olefin.

The isolated complexes were characterized by IR and ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy. The two IR bands at about 1560 and 1600 cm^{-1} in the spectra of **4** and **5** indicate the coordination of the PNP ligand,[10] and as also found for complexes **1**−**3**, the fact that both BF_4^- anions are not coordinated is suggested by the bands at 1052 and 1060 cm^{-1} which were observed for **4** and **5**, respectively.[11]

In the ^{31}P NMR spectra a singlet appears at δ 51.3 for **4** and at δ 47.0 for **5**. These signals are shifted downfield compared to those for the corresponding Rh(I) complexes (δ 38.2 and δ 41.7, respectively), in agreement with the higher positive charge on the metal ion. They are also shifted by about 10 ppm downfield compared to those for the N-donor ligand complexes **1**−**3**, most likely as a consequence of the weaker donor character of the olefinic double bond compared to that of nitrogen. This is consistent with the feature found for the corresponding PNP rhodium(I) complexes.[2]

While in the ^{1}H NMR spectrum of the ethylene complex **4** the characteristic virtual triplet for the methylene protons of the PNP ligand is found at δ 4.91, the typical signal pattern of an AA′BB′XX′ spin system is observed for these protons of the complex **5** which consists of two doublets of virtual triplets at δ 4.79 and 4.91 with a coupling constant of $J_{H_a-H_b} = 17.0$ Hz. Since in the ^{13}C and ^{31}P spectra only one signal is observed for corresponding nuclei in the symmetry-related halves of the PNP ligand, this indicates the collapse of the C_{2v} symmetry of the $[Pd(PNP)]^{2+}$ fragment to a C_2 symmetry. This in turn indicates that, under the conditions of the spectral runs (25 °C, anhydrous CD_2Cl_2), the coordinated styrene molecule rotates freely around the Pd−double-bond axis but does not undergo (on the NMR frequency scale) rapid exchange with the free ligand, whose traces are indeed observable in the spectrum. The last observation seems to be uncommon for 16 e^- olefin complexes of Pd(II), which in most cases give averaged resonances even at low temperature,[11] and indicates a lower than usual lability of the coordinated olefin, probably arising from steric reasons (see later). The ^{1}H and ^{13}C shifts of the olefinic protons and carbons in the two complexes **4** and **5** are listed in Table 1, in comparison to those of the corresponding Rh(I) complexes and to those of the free olefins. As seen from Table 1, the olefin signals of complexes **4** and **5** are strongly shifted downfield compared to those for the corresponding Rh(I) complexes, although they still appear at substantially higher field compared to the free olefin. Furthermore, while in the case of the Rh(I) styrene complex the shift difference between the terminal carbon C(1) and the methyne carbon C(2) is essentially the same as for the free olefin, this difference almost doubles in the case of the Pd(II) complex **5** (that is, the methyne carbon C(2) undergoes a much larger downfield shift than the terminal carbon C(1) on going from Rh^+ to Pd^{2+}). The proton signals follow the same trend. Even if the ^{13}C chemical shifts of π-bonded olefins can be only partly correlated with the extent of σ and π contributions to the metal−olefin bond,[12] these downfield shifts are consistent with the increased positive charge of the central ion and with the consequent strong decrease in π back-donation that is expected, all the coordination environments being the same. In the styrene complex **5**, the larger downfield shift observed for the methyne carbon C(2) suggests a larger fractional positive charge on this atom than in the free olefin (and in the Rh^+ complex). This suggests some unsymmetrical bonding of the olefin, where the methyne carbon is farther away from the metal and is positively charged,[12,13] as is indeed confirmed by the X-ray structural analysis of complex **5**.

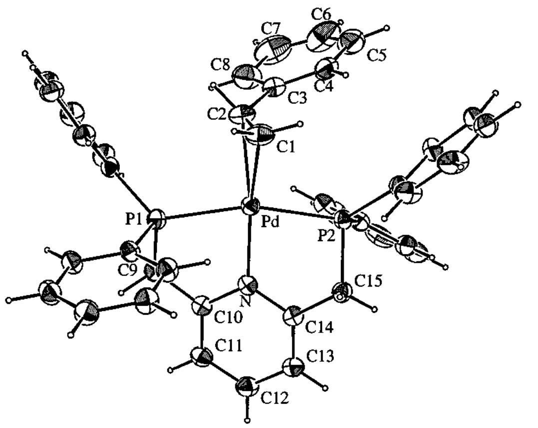

Figure 1. ORTEP view of the complex dication of **5**. Thermal ellipsoids are drawn at the 50% probability level.

The ^{13}C NMR signals of the olefinic carbons of styrene are also strongly downfield shifted in comparison to those found for the cationic palladium(II) complex $[Pd(C_5H_5)\{P(n\text{-}C_4H_9)_3\}(CH_2{=}CHPh)]ClO_4$ (δ 56.2 and 92.1).[12] It is worth noting that for the latter complex not only the lower positive charge but also the coordinative saturation[12] contributes to the lower values of the ^{13}C δ's.

Molecular Structure of $[Pd(PNP)(CH_2{=}CHPh)](BF_4)_2$ (5). Single crystals of the title compound, suitable for X-ray analysis, were obtained from a concentrated solution in dichloromethane containing an excess of styrene after standing at −20 °C for a few days. An ORTEP view of the complex dication is shown in Figure 1. Selected bond lengths and angles are collected in Table 2. The molecule displays the usual square-planar coordination around the palladium center (apart from the two bite angles P−Pd−N (81.2°), which are con-

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for [Pd(PNP)(CH$_2$=CHR)](BF$_4$)$_2$ (5)

Pd−P(1)	2.314(1)	Pd−P(2)	2.330(2)	Pd−N	2.058(4)
Pd−C(1)	2.165(7)	Pd−C(2)	2.273(7)	C(1)−C(2)	1.292(10)
P(1)−C(1)	1.832(6)	P(2)−C(15)	1.840(5)		
P(1)−Pd−P(2)	162.4(1)	P(1)−Pd−N	81.2(2)	P(2)−Pd−N	81.2(2)
N−Pd−C(1)	159.3(4)	N−Pd−C(2)	166.5(4)	C(1)−Pd−C(2)	33.7(4)
C(1)−C(2)−C(3)	128.1(11)	Pd−C(2)−C(3)	111.5(8)		

strained to be smaller than 90°), and its overall geometry is quite similar to that of the corresponding Rh(I) complex,[2] indicating that the steric constraints imposed by (and acting on) the coordinated PNP ligand largely dominate the effects of packing forces. Thus, the pyridine ring forms an angle of 21° (20° in the Rh(I) complex) with the coordination plane defined by P(1), N, P(2), and Pd, and the styrene double bond is tilted by 15° from the normal to the coordination plane (16° in the Rh(I) complex). The tilting of the double bond appears to arise in both cases from the need to avoid a close steric contact between the styrene phenyl ring and the equatorial phenyl group on P(2).

It is particularly interesting to compare the metal−ligand bond distances with those of the corresponding Rh(I) complex,[2] because the two molecules are isoelectronic and isostructural (when packing is not considered). The comparison shows small but significant differences appearing in a clear and consistent pattern. The Pd−N distance (2.058(4) Å) is shorter than the Rh−N distance by 0.04 Å, while the average Pd−P distance (2.32 Å) is longer than the average Rh−P distance by 0.03 Å. The Pd−C(1) and Pd−C(2) distances (2.165(7) and 2.273(7) Å, respectively) are longer than the corresponding Rh−C distances by 0.03 and 0.07 Å, respectively. Thus, the increase of the central ion charge increases the bond strength with the almost purely donor pyridine nitrogen but reduces the bond strength with ligands having π-acceptor ability (the phosphine and, especially, the C=C double bond). The greater elongation (relative to the Rh(I) complex) observed for Pd−C(2) bond compared to the Pd−C(1) is consistent with the larger downfield shift observed for the C(2) carbon. Thus, increasing the charge of the central ion causes the olefin to slip toward a less symmetrical bonding, with an increased difference between the two Pd−C bond lengths. Such slipping was also observed in Pd(II)[14] and Pt(II)[15] complexes of para-substituted styrenes, as the result of the presence of electron-releasing substituents. Apparently, the asymmetry in the styrene bonding to the metal can be increased by all the factors which are expected to increase the relative importance of the σ-donor component of the olefin−metal bond compared to the π-back-donation.

The bonding parameters of the [Pd(PNP)]$^{2+}$ fragment in the styrene complex **5** are approximately identical with those found in the analogous triethylphosphine complex [Pd(PNP)(PEt$_3$)](BF$_4$)$_2$.[7] Only the Pd−N distance is significantly shorter in the complex **5** (2.058(4) Å) than that observed in the triethylphosphine complex (2.107(4) Å). This may be explained by the weaker σ-donor ability of the C=C double bond in comparison to the phosphine donor.

The C(1)−C(2) double-bond distance (1.29(1) Å) is the shortest ever reported for Pd(II) and Pt(II) styrene complexes, perhaps too short to be realistic. Nevertheless, even allowing in this case for an error 3−4 times larger than the standard deviation of 0.01 Å (formal standard deviations are notoriously fairly optimistic), the C=C double bond is not longer than expected for the free olefin and definitely is much shorter than in the corresponding Rh$^+$ complex (1.383(7) Å). Again, this is consistent with a much lower (if any) metal to olefin π-back-donation expected for the Pd^{2+} complex.

Reactivity of the Palladium(II) Olefin Complexes 4 and 5 toward Secondary Amines. The nucleophilic addition of amines to a simple monoolefin coordinated to Pt(II) or Pd(II) in 16 e$^-$ complexes is well-known.[5,6] However, while in the case of Pt(II) a broad range of complexes has been found to be reactive,[5,16,17] not many examples of such a reaction have been reported in the case of Pd(II).[6] Indeed, Pd(II) olefin complexes are less stable and more labile than corresponding Pt(II) complexes, and therefore an amine is likely to give in most cases a substitution reaction rather than a nucleophilic addition.

Theoretical[18] and experimental[17] studies indicate that cationic species are more reactive toward nucleophilic attack than neutral complexes. Accordingly, the dicationic complexes **4** and **5** would be expected to be very reactive. On the other hand, the high positive charge of dicationic complexes is also expected to favor a substitution reaction, both thermodynamically and kinetically, and therefore the outcome of the reactions of **4** and **5** with secondary amines is not easily predictable in advance.

The ethylene complex **4** does indeed react with a 4-fold excess of piperidine in dichloromethane at −78 °C, giving the corresponding palladium(II) β-aminoethyl complex **6** (cf. Scheme 1). This addition product, which was isolated as a beige solid, could not be purified by recrystallization. However, the ^{1}H NMR spectrum of the crude product is quite consistent with the expected structure of **6** (see Experimental Section). A solution of **6** upon standing for 4 days at room temperature was analyzed by gas chromatography, which showed no β-H-elimination product. Upon reductive degradation of the complex **6** with NaBH$_4$ in THF ethylpiperidine was obtained in a yield of 78%, which was detected by ^{1}H NMR and GC analysis. Other products could not be detected.

The nucleophilic attack of dimethylamine on the styrene complex **5** also occurred. However, even at −78 °C the substitution reaction could not be suppressed completely (cf. Scheme 2). The ^{1}H NMR spectrum of

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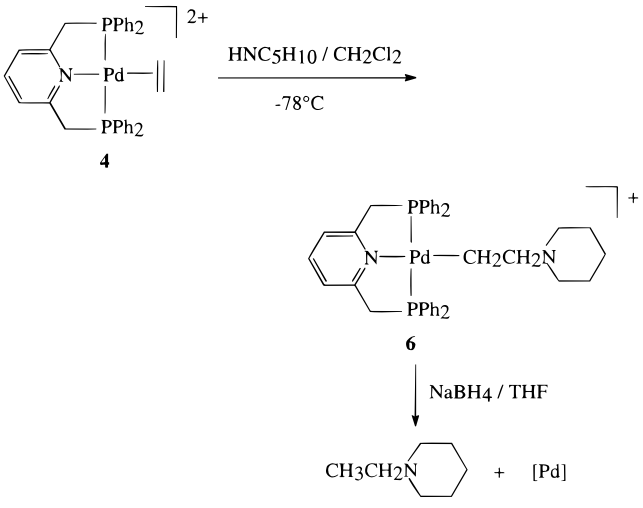
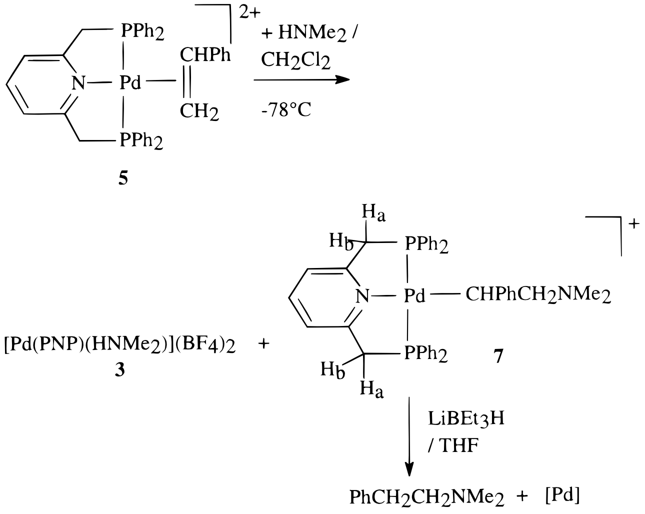
Scheme 1



Scheme 2



the isolated solid exhibits the typical AA′BB′XX′ signal pattern at δ 4.23 and 4.48 ($J_{H_a-H_b}$ = 16.8 Hz) for the nonequivalent methyl protons of the PNP ligand and a singlet at δ 2.27 for the dimethylamino group which can be assigned to the addition product **7**; in addition, the signals of the amine complex **3** were observed in a ratio of ca. 4:1 (**7**:**3**). Also, no indication for a β-H elimination could be observed when a solution of the resulting solid in CH_2Cl_2 was stored over 4 days at room temperature.

The mixture of the complexes was used directly for the reductive degradation with $LiBEt_3H$ in THF. In the ether extract not only $PhCH_2CH_2NMe_2$ (in a yield of 21%) but also the corresponding quaternary ammonium salt $(PhCH_2CH_2)_2NMe_2^+$ was detected by ^1H NMR spectroscopy in about 30% molar ratio. Obviously a nucleophilic attack of complex **7** at the π-coordinated styrene in **5** is responsible for the formation of the ammonium salt. Such multiple addition was also observed in the case of the platinum(II) β-aminoethyl complexes.[19] The regiochemistry of the products indicates an anti-Markovnikov attack on the coordinated styrene, which is opposite to what observed for a neutral Pt(II) complex.[16] The anti-Markovnikov attack is somewhat unexpected, not only because it is in contrast to what is observed in the case of Pt(II) but also because the ^{13}C shift data suggest a fractional positive charge on the methyne carbon C(2) relative to C(1). It should be kept in mind, however, that the regiochemical results of amine addition to unsaturated ligands have to be taken with some caution, since reversibility and thus equilibration of the product mixture are possible.[20] Nevertheless, under the hypothesis of a kinetic control of the recaction, its regiochemistry can be reasonably explained on steric grounds, by considering the optimized geometry of the transition state for the nucleophilic addition.[18] It is seen that in the case of attack at C(2) the styrene phenyl ring would be pushed toward the metal, thus interacting sterically with the proximal phenyl group on the phosphine ligand and raising the energy of the transition state. On the other hand, in the case of attack at C(1) the styrene phenyl ring is pushed *away* from the metal, and no additional barrier is added to the reaction, which would explain the observed regiochemistry.

Conclusion

The results reported in this paper show that dicationic palladium(II) complexes of the type $[Pd(PNP)L](BF_4)_2$ can be obtained both with N-donor ligands (L = CH_3CN, pyridine, Me_2NH) and with olefins (L = C_2H_4, $PhCH{=}CH_2$), by removing the chloride ions from $Pd(PNP)Cl_2$ with 2 equiv of silver salt under appropriate conditions. The comparison of their NMR and X-ray diffraction data with those of the isoelectronic and isostructural Rh(I) complexes[2,3] shows a number of consistent differences resulting from the increased nuclear charge. Among these, large downfield ^{13}C shifts of the olefinic carbons, significantly longer metal–olefin bond distances, and a significantly shorter C=C distance in the π-coordinated styrene were found, reflecting a somewhat weaker bond and a strongly decreased back-donation in the dicationic palladium(II) complex. In addition, in comparison to their rhodium(I) analogues, complexes **1**–**5** are less stable both in air as solids and in solution, consistent with the expected higher tendency to undergo hydrolysis. If it is considered that complexes **4** and **5** are the first dicationic monoolefin palladium(II) complexes to be described, their very existence as isolable species suggests that the PNP ligand might have a role in their stabilization. A stabilizing factor could possibly be a steric protection against substitution reactions exerted by the proximal P-phenyl groups protruding on each side of the coordinated olefin. Indeed, no fast exchange was observed with the free olefin in the NMR spectra at room temperature, an uncommon feature for 16 e^- Pd(II) olefin complexes. Since coordination at the $Pd(PNP)^{2+}$ fragment strongly increases the electrophilic character of the olefin compared to that of the corresponding $Rh(PNP)^+$ species, they are susceptible to nucleophilic attack by secondary amines, probably with the help of the above-mentioned moderate inertness to substitution. Unfortunately, as long as the target is a catalytic hydroamination, the palladium(II) species are not fa-

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[19] De Renzi, A.; Paiaro, G.; Panunzi, A.; Paolillo, L. *Gazz. Chim. Ital.* **1972**, *102*, 281.

[20] (a) Bäckvall, J.-E.; Björkman, E. E. *Acta Chem. Scand.* **1984**, *B38*, 91. (b) Åkermark, B.; Vitagliano, A. *Organometallics* **1985**, *4*, 1275.

vored, since the Pd−C σ-bond in the β-aminoethyl complexes is too stable to be cleaved protolytically under the reaction conditions and can only undergo reductive cleavage with irreversible destruction of the complex. Nevertheless, the present study shows the possibility of isolating dicationic monoolefin complexes of palladium(II), opening the way to further investigations on the synthesis and properties of a class of compounds which are expected to be highly reactive.

Experimental Section

General Comments. All reactions were carried out under dry argon or ethylene. All solvents were dried, degassed, and distilled before using. Acetone, piperidine, CD_2Cl_2, $CDCl_3$, and acetone-d_6 were refluxed over 4 Å molecular sieves and degassed by bubbling argon. Styrene was distilled under reduced pressure before use. Diethyl ether and THF were refluxed over Na/benzophenone. $AgBF_4$ and $NHMe_2$ were obtained from Fluka and used without further purification.

Infrared spectra were recorded in Nujol on a Philips Analytical PU9600 FTIR spectrometer. The ^1H NMR spectra were recorded at 200 MHz on a Varian XL-200, at 270 MHz on a Bruker AC-270, or at 300 MHz on a Varian Gemini 300 NMR spectrometer. The $^{31}P\{^1H\}$ NMR spectra were recorded at 121 MHz and the $^{13}C\{^1H\}$ NMR spectra at 75 MHz on a Varian Gemini 300 NMR spectrometer. The ^1H 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. A Chrompack CP 9000 gas chromatograph was used for the identification of liquid organic compounds. Elemental analyses of C, H, and N were carried out on a LECO CHN 932 analyzer.

X-ray Data Collection and Reduction. X-ray data were collected from a prismatic crystal covered with glue at room temperature on an Enraf-Nonius CAD4-F automatic diffractometer using Cu Kα graphite-monochromated radiation and operating in the ω/θ scan mode. The unit cell parameters were obtained by a least-squares fitting of the setting values of 25 strong reflections in the θ range $24 \le \theta \le 29°$. Three monitoring reflections, measured every 500 reflections, showed insignificant intensity fluctuations. The structure was solved by the heavy-atom method. At the end of the isotropic refinement a correction for absorption effects was applied according to Walker and Stuart[21] by using the computer program DIFABS (maximum and minimum values of the absorption correction were 1.20 and 0.65). The full-matrix least-squares refinement minimized the quantity $\sum w(\Delta F)^2$ with $w^{-1} = [\sigma^2(F_o) + (0.02F_o)^2 + 0.8]$, where σ is derived from counting statistics. All non-hydrogen atoms were refined anisotropically. H atoms, placed in calculated positions, were assigned the isotropic equivalent thermal parameters of the carrier atoms and included in the final refinement as riding atoms. The final Fourier difference map showed no peaks greater than 0.76 e Å^{-3}. The largest shift-to-esd ratio in the final cycle was 0.02.

All calculations, carried out on a Vax 750 at the *Centro Interdipartimentale di Metodologie Chimico-fisiche* of the University of Naples, were performed by using the Enraf-Nonius (SDP) set of programs.[22]

Final atomic coordinates, full lists of bond distances and angles, hydrogen atom parameters, and anisotropic thermal parameters of the non-hydrogen atoms have been deposited as Supporting Information. Crystal data, data collection conditions, and solution and refinement details are given in Table 3.

Table 3. Crystal Data, Data Collection Conditions, and Solution and Refinement Details for [Pd(PNP)(CH$_2$=CHPh)](BF$_4$)$_2$ (5)

cryst size/mm	0.10 × 0.20 × 0.30
formula	$PdP_2F_8NC_{39}B_2H_{35}$
fw	859.7
cryst syst	monoclinic
space group	$P2_1/c$
a/Å	13.930(5)
b/Å	12.040(4)
c/Å	22.665(5)
β/deg	94.85(2)
V/Å^3	3788(3)
Z	4
F(000)	1736
D_m/g cm^{-3}	1.50
D_c/g cm^{-3}	1.51
λ(Cu Kα)/Å	1.540 56
θ_{max} (deg)	72
μ/cm^{-1}	54.6
no. of indep rflns	7454
no. of rflns above $3\sigma(I)$	4715
no. of refined params	478
goodness of fit	0.800
R	0.046
R_w	0.050

Syntheses. Pd(PNP)Cl_2 was prepared according to the procedure described in the literature.[8]

[Pd(PNP)(MeCN)](BF$_4$)$_2$ (1) and [Pd(PNP)(py)](BF$_4$)$_2$ (2). To a suspension of 100 mg (0.153 mmol) of Pd(PNP)Cl_2 in 3 mL of CH_2Cl_2 and 0.5 mL of acetonitrile (**1**) or pyridine (**2**) was added 60 mg (0.31 mmol) of $AgBF_4$. After the dissolution of the starting complex, silver chloride precipitated. The silver chloride was filtered off, and the volume of the solution was reduced to 1.5 mL. The acetonitrile complex **1** crystallized as a pale yellow solid upon dropwise addition of 1 mL of diethyl ether and standing for 2−3 h at −20 °C. The pyridine complex **2** precipitated as an ivory-colored crystalline solid when 8 mL of diethyl ether was added slowly to the filtrate. The products were filtered off, washed two times with diethyl ether, and dried under vacuum.

1: yield 93 mg (0.115 mmol, 76%); dec pt 140−150 °C. Anal. Calcd for $C_{33}H_{30}B_2F_8N_2P_2Pd$: C, 49.76; H, 3.80; N, 3.52. Found: C, 49.77; H, 4.36; N, 3.40. ^{31}P NMR (CD_2Cl_2): δ 36.1 (s). ^1H NMR (CD_2Cl_2): δ 2.25 (s, 3H, CH_3), 4.66 (vt, $^2J_{P-H} + {}^4J_{P-H} = 5.3$ Hz, 4H, CH_2), 7.67 (m, 12H, Ph), 7.74 (d, 2H, J_{H-H} =7.8 Hz, py), 7.96−8.03 (m, 8H, Ph), 8.26 (t, 1H, $^2J_{H-H} = 7.8$ Hz, py). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 3.8 (s, CH_3), 42.4 (vt, $^1J_{P-C} + {}^3J_{P-C} = 14.3$ Hz, CH_2), 124.4 (vt, $^1J_{P-C} + {}^3J_{P-C} = 7.5$ Hz, py-3,5), 129.4 (br, CN), 130.4 (vt, $^1J_{P-C} + {}^3J_{P-C} = 5.5$ Hz, Ph_m), 133.2 (vt, $^1J_{P-C} + {}^3J_{P-C} = 7.1$ Hz, Ph_o), 133.7 (s, Ph_p), 143.2 (s, py-4), 162.9 (vt, $^1J_{P-C} + {}^3J_{P-C} < 3$ Hz, py-2,6). IR (Nujol): ν(py), 1576 and 1603; ν(BF_4), 1058; ν(CN), 2305 and 2340 cm^{-1}.

2: yield 128 mg (0.153 mmol, 100%); dec pt 132 °C. Anal. Calcd for $C_{36}H_{32}B_2F_8N_2P_2Pd$: C, 51.81; H, 3.86; N, 3.36. Found: C, 51.42; H, 3.87; N, 3.36. ^{31}P NMR (acetone-d_6): δ 38.3 (s). ^1H NMR (acetone-d_6): δ 5.14 (vt, 4H, $^2J_{P-H} + {}^4J_{P-H} = 5.2$ Hz, CH_2), 7.52−7.57 (m, 12H, Ph), 7.63−7.78 (m, 8H, Ph, py), 7.95 (d, 2H, $J = 7.7$ Hz, py), 8.05 (t, 1H, $J = 7.7$ Hz, py), 8.24 (t, 1H, $J = 7.8$ Hz, py[PNP]), 8.82 (d, 2H, $J_{H-H} = 5.2$ Hz, py). ^{13}C NMR (CD_2Cl_2): δ 41.8 (vt, $^1J_{P-C} + {}^3J_{P-C} = 13.3$ Hz, CH_2), 124.2 (vt, $^1J_{P-C} + {}^3J_{P-C} = 6.7$ Hz, py-3,5[PNP]), 127.3 (s, py-3,5), 130.1 (vt, $^1J_{P-C} + {}^3J_{P-C} = 5.4$ Hz, Ph_m), 132.8 (s, Ph_p), 133.2 (vt, $^1J_{P-C} + {}^3J_{P-C} = 7.1$ Hz, Ph_o), 139.8 (s, py-4), 143.4 (s, py-4), 151.8 (s, py-2.6), 162.0 (vt, $^1J_{P-C} + {}^3J_{P-C} = 3$ Hz, py-2,6[PNP]). IR (Nujol): ν(py), 1566 and 1603; ν(BF_4), 1057 cm^{-1}.

[Pd(PNP)(NHMe$_2$)](BF$_4$)$_2$ (3). To a solution of 317 mg (0.398 mmol) of [Pd(PNP)(CH_3CN)](BF_4)$_2$ in 4 mL of CH_2Cl_2 was added 5 mL of a ca. 1 M solution of dimethylamine in CH_2Cl_2 at −78 °C. The solution was stirred for 10 min and

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(21) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

(22) Enraf-Nonius CAD-4 Software, Version 5.0; Enraf-Nonius, Delft, The Netherlands, 1989.

warmed to 0 °C. At this temperature the volume of the solution was reduced to 1.5 mL. A beige solid precipitated upon addition of diethyl ether. The solid was filtered off, washed with diethyl ether, and dried under vacuum. The product could not be purified by recrystallization due to its poor stability in solution.

Yield: 175 mg (0.218 mmol, 55%). Dec pt 116 °C. ^{1}H NMR ($CDCl_3$): δ 2.44 (d, 3H, $^3J_{H-H}$ = 5.6 Hz, NCH_3), 3.9 (br, 1H, HN), 4.68 (vt, 4H, $^2J_{P-H} + {}^4J_{P-H}$ = 5.0 Hz, CH_2), 7.63 (m, Ph), 7.97 (m, Ph) (the d and t of pyridine overlapped by a broad signal of an impurity as well as by Ph multiplets). IR (Nujol): ν(py), 1568 and 1610; $\nu(BF_4)$, 1058 cm^{-1}.

[Pd(PNP)(C_2H_4)](BF_4)$_2$ (4). A suspension of 1.01 g of Pd(PNP)Cl_2 (1.55 mmol) and 602 mg of $AgBF_4$ (3.10 mmol, 2 equiv) in 20 mL of CH_2Cl_2 was cooled to −78 °C and stirred for 5 min under ethylene. Upon warming, the mixture was stirred for 10 min at room temperature. The precipitated AgCl was filtered off, and the ivory-colored product crystallized by slow dropping of ca. 70 mL of diethyl ether with stirring of the solution. The product was filtered off, washed with diethyl ether, and dried under vacuum.

Yield: 1.0 g (1.28 mmol, 83%). Dec pt: 134−138 °C. Anal. Calcd for $C_{33}H_{31}B_2F_8NP_2Pd$: C, 50.58; H, 3.99; N, 1.79. Found: C, 50.49; H, 4.36; N, 1.77. ^{31}P NMR (CD_2Cl_2): δ 51.3 (s). ^{1}H NMR (CD_2Cl_2): δ 4.49 (s, 4H, C_2H_4), 4.91 (vt, 4H, $^2J_{P-H} + {}^4J_{P-H}$ = 5.4 Hz, CH_2), 7.62−7.73 (m, 14H, Ph and py), 7.79−7.86 (m, 8H, Ph), 7.92 (t, 1H, J_{H-H} = 7.6 Hz, py). ^{13}C NMR (CD_2Cl_2): δ 44.5 (vt, $^1J_{P-C} + {}^3J_{P-C}$ = 13.6 Hz), 88.0 (s, C_2H_4), 123.9 (vt, $^1J_{P-C} + {}^3J_{P-C}$ = 7.0 Hz, py-3,5), 130.4 (vt, $^1J_{P-C} + {}^3J_{P-C}$ = 6.0 Hz, Ph_m), 133.6 (vt, $^1J_{P-C} + {}^3J_{P-C}$ = 6.6 Hz, Ph_o), 134.0 (s, Ph_p), 143.4 (s, py-4), 160.1 (vt, $^1J_{P-C} + {}^3J_{P-C}$ = 3 Hz, py-2,6). IR (Nujol): ν(py), 1564 and 1622; $\nu(BF_4)$, 1052 cm^{-1}.

[Pd(PNP)($CH_2{=}CHPh$)](BF_4)$_2$ (5). To a suspension of 300 mg (0.459 mmol) of Pd(PNP)Cl_2 in 10 mL of CH_2Cl_2 and 1 mL of styrene was added 180 mg (0.925 mmol) of $AgBF_4$. The mixture was stirred for 10 min. The precipitated silver chloride was filtered off, and the volume of the solution was reduced to 1.5 mL. The solution was stored for 30 min at −20 °C. The yellow crystalline product was filtered off, washed three times with diethyl ether and dried under vacuum.

Yield: 320 mg (0.372 mmol, 81%). Dec pt: 140−150 °C. Anal. Calcd for $C_{39}H_{35}B_2F_8NP_2Pd$: C, 54.49; H, 4.10; N, 1.63. Found: C, 54.63; H, 4.18; N, 1.61. ^{31}P NMR (CD_2Cl_2): δ 47.0 (s). ^{1}H NMR (CD_2Cl_2): δ 4.46 (m, 1H, styrene), 4.79 (dvt, 2H, $^2J_{H_a-H_b}$ = 17.0 Hz, $^2J_{P-H} + {}^4J_{P-H}$ = 4.9 Hz, PCH_a), 4.91 (vt, 2H, $^2J_{H_a-H_b}$ = 17.0 Hz, $^2J_{P-H} + {}^4J_{P-H}$ = 5.4 Hz, PCH_b), 5.16 (d, 1H, J_{H-H} = 8.6 Hz, styrene), 6.56 (m, styrene), 6.79 (d, J_{H-H} = 7.6 Hz, PPh_o, styrene), 7.15 (t, J_{H-H} = 7.7 Hz, PPh_m, styrene), 7.33 (t, J_{H-H} = 7.5 Hz, PPh_p, styrene), 7.51−7.88 (m, PPh and py). ^{13}C NMR (CD_2Cl_2): δ 44.4 (vt, $^1J_{P-C} + {}^3J_{P-C}$ = 13.2 Hz), 77.2 (s, styrene), 120.2 (s, styrene), 123.9 (vt, $^1J_{P-C} + {}^3J_{P-C}$ = 5.8 Hz, py-3,5), 128.6 (s, styrene), 130.4 (vt, $^1J_{P-C} + {}^3J_{P-C}$ = 5.3 Hz, Ph_m), 130.5 (vt, $^1J_{P-C} + {}^3J_{P-C}$ = 5.2 Hz, $Ph_{m'}$), 133.3 (s, styrene), 133.9 (vt, $^1J_{P-C} + {}^3J_{P-C}$ = 6.4 Hz, Ph_o), 134.0 (vt, $^1J_{P-C} + {}^3J_{P-C}$ = 6.5 Hz, $Ph_{o'}$), 134.1 (s, Ph_p), 143.4 (s, py-4), 159.9 (vt, $^1J_{P-C} + {}^3J_{P-C}$ < 3 Hz, py-2,6). IR (Nujol): ν(py), 1560 and 1600; $\nu(BF_4)$, 1060 cm^{-1}.

Reaction of 4 with Piperidine. A 345 mg amount of [Pd(PNP)(C_2H_4)](BF_4)$_2$ (0.440 mmol) was dissolved in 3 mL of CH_2Cl_2; this solution was cooled to −78 °C, and 175 μL of piperidine (ca. 4 equiv) was added. The reaction mixture changed color immediately to brown. After the mixture was stirred for 1 h at −78 °C, the solvent was removed under vacuum while cold. A beige solid was obtained, which was recrystallized two times from CH_2Cl_2/diethyl ether. However, after the second recrystallization some brown impurities maintained (205 mg, 60% yield). The isolated product was identified by ^{1}H NMR spectroscopy ($CDCl_3$) as [Pd(PNP)($CH_2CH_2NC_5H_{10}$)]BF_4 (**6**): δ 1.35−1.62 (m's, $H_{\beta,\gamma}$ of piperidine ring), 1.89 (m, PdCH_2CH$_2$), 2.36 (m, H_α of piperidine ring), 2.75 (m, PdCH$_2$CH_2), 4.44 (vt, $^2J_{P-H} + {}^4J_{P-H}$ = 4.1 Hz, PCH_2), 7.48−7.61 (m, Ph, py), 7.63−7.76 (m, Ph).

Reductive Degradation of 6. A 205 mg amount of [Pd(PNP)($CH_2CH_2NC_5H_{10}$)]BF_4 (**6**) (0.26 mmol) was suspended in 5 mL of THF. A 40 mg (1.06 mmol) portion of $NaBH_4$ was added to the suspension at −78 °C. The mixture was warmed to room temperature and stirred for 1 h. A 4 mL amount of diethyl ether and 2 mL of 2 M HCl were added at 0 °C. After the mixture was stirred for 1 h, the aqueous layer was separated and NaOH added. The basic aqueous phase was extracted two times with 4 mL of diethyl ether and dried over Na_2SO_4. The solvent was removed from the ether extract under reduced pressure. A 26 mg amount of a pale yellow oil was obtained, which was identified as ca. 90% pure ethylpiperidine by ^{1}H NMR and GC analysis (yield 78%).

Reaction of 5 with $NHMe_2$ and Reductive Degradation. A 300 mg amount of [Pd(PNP)($CH_2{=}CHPh$)](BF_4)$_2$ (0.35 mmol) was dissolved in 3 mL of CH_2Cl_2, and this solution was cooled to −78 °C. A 2 mL portion of a solution of $NHMe_2$ in CH_2Cl_2 (ca. 1 M, 5−6 equiv, ca. 1.9 mmol, also cooled to −78 °C) was added. The reaction mixture changed color to pale brown and was stirred for 30 min at −78 °C. The solvent was removed under vacuum at the same temperature, leaving a beige microcrystalline solid. The crude product could not be purified by recrystallization. The solid was characterized as such by ^{1}H NMR spectroscopy ($CDCl_3$): δ 2.27 (s, NMe_2), 3.26 (m, PdCHPhCH$_2$), 3.78 (m, PdCHPhCH_2), 4.23 (dvt, $^2J_{P-H} + {}^4J_{P-H}$ = 4.7 Hz, J_{H-H} = 16.8 Hz, PCH_a), 4.48 (dvt, $^2J_{P-H} + {}^4J_{P-H}$ = 3.1 Hz, J_{H-H} = 16.8 Hz, PCH_b), 6.28 (d, J = 15.0 Hz, PdCHPh), 6.85 (m, PdCHPh), 7.29−7.68 (m, Ph, py), 7.93 (m, Ph). In addition, the signals of **3** appear in this spectrum. For the reductive degradation this solid was used directly.

The crude product (containing ca. 0.93 mmol of palladium) was suspended in 5 mL of THF and the suspension cooled to −45 °C. Upon addition of 1 mL of a solution of 1.0 M $LiBEt_3H$ in THF to the suspension the mixture changed color immediately to brown and was stirred for 30 min at −45 °C. The mixture was warmed to room temperature and stirred for 30 min. A 10 mL amount of diethyl ether and 5 mL of 2 M HCl were added at 0 °C. After the mixture was stirred for 1 h, the aqueous layer was separated and NaOH added. The basic aqueous phase was extracted two times with 4 mL of diethyl ether and dried over Na_2SO_4. The diethyl ether of the extract was removed under vacuum, leaving a brown-yellow oil which was identified by ^{1}H NMR spectroscopy as a mixture of $PhCH_2CH_2NMe_2$ and $(PhCH_2CH_2)_2NMe_2^+$ (in a ratio of about 2:1). The yield of $PhCH_2CH_2NMe_2$ was 21%, as found by GC analysis. Other isomers were not detected. The chemical shifts and retention time were compared to those of authentic samples prepared according to the procedure in ref 23.

Acknowledgment. An ERASMUS visiting scholarship for C.H. at the University of Napoli, May−July 1996, is acknowledged. We thank the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 347 of the University of Würzburg) and the Italian National Research Council (CNR) for financial support.

Supporting Information Available: Tables of the complete set of crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, all bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters (7 pages). Ordering information is given on any current masthead page.

OM970699Q

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(23) von Braun, J. *Chem. Ber.* **1910**, *43*, 3209.