Versatility of Iminophosphoranes and Noninnocent Behavior of the 1,5-Cyclooctadiene Ligand in Palladium(II) Complexes. Synthesis of σ-Allyl Derivatives

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The treatment of $PdCl_2(NCPh)_2$ with $Ph_3P{=}NPh$ (**1**) gives the expected complex *trans*-$PdCl_2[N(Ph)PPh_3]_2$ (**3**). However, the reaction of $PdCl_2(COD)$ (COD = 1,5-cyclooctadiene) with **1** or $Ph_3P{=}N$-1-Np (**2**) (Np = naphthyl) occurs through nucleophilic attack of **1** or **2** on one olefinic bond of the COD ligand followed by proton abstraction on the adjacent methylene group, giving the η^1-allyl complexes $[Ph_3P(R)NH\cdots Cl_2Pd(C_8H_{11})]$ (R = Ph, **4**; Np, **5**). The X-ray structure of **4** has been determined and shows two interesting facts: (i) the η^1-η^2-bonded cyclooctadienyl ligand, containing a η^1-allyl fragment, and (ii) the presence of a strong H bond between one of the Cl ligands and the proton of the NH group. This H bond persists in solution, as shown by NMR and molar conductance measurements. The abstraction of a chloride on **4** by reaction with $AgClO_4$ cleaves the H bond and gives a mixture of the salt $[Ph_3PN(H)Ph](ClO_4)$ (**6**) and the neutral η^1-η^2-cyclooctadienyl complex $[Pd(\mu\text{-}Cl)(C_8H_{11})]_2$ (**7**). Complex **7** is an adequate precursor for the synthesis of other stable η^1-allyl complexes, and no $\eta^1-\eta^3$ allyl interconversion has been observed.

Introduction

Reactions that form C−C and C−X bonds (X = heteroatom) through nucleophilic attack on a C=C or a C≡N bond, activated by bonding to a transition metal, are versatile and powerful synthetic tools.[1] Nucleophilic addition to Pd-coordinated alkenes[2] is a very well-known reaction with important implications in industrial processes. Among the different olefins and diolefins, 1,5-cyclooctadiene (COD) has been one of the most studied systems, due to its versatility and due also to the wide variety of bonding modes obtained.[3] Stabilized phosphorus ylides are a particular class of nucleophiles, and they have shown a clear reactivity toward alkenes bonded to Pd(II) and Pt(II) centers,[4a,b] as a result of which the corresponding σ-alkyl complexes have been formed. This reactivity has been recently applied to other substrates as nucleophiles.[4c] Coordinated nitriles are also adequate precursors for C−C and C−X couplings, and a wide reactivity is being developed at the present time.[5] For instance, 1,3-diazadienes,[5a] imines,[5c] and 1,2,4-oxadiazolines[5e] can be obtained by reaction of the appropriate precursor with Pd(II)- or Pt(II)-bonded nitriles. In addition, it is also possible to modulate their reactivity depending on whether they are coordinated or not to the metal, for instance in species such as RCH_2CN.[5b] Phosphorus ylides are also able to react with bonded nitriles, and some notable results have been reported.[6]

In line with these results, a recent contribution shows that iminophosphoranes are also able to react with Pt-bonded nitriles.[7] Iminophosphoranes are species of general structure $R_3P{=}NR'$ (R, R′ = alkyl, aryl, etc.), which show a very rich coordination chemistry.[8,9] Aiming to expand the scope of the use of iminophosphoranes as nucleophiles in C−N bond forming reactions, we have probed the reactivity of $Ph_3P{=}NPh$ (**1**) and $Ph_3P{=}NNp$ (**2**) (Np = naphthyl) toward Pd(II) precursors, such as $PdCl_2(NCR)_2$ (R = Me, Ph) and $PdCl_2(COD)$. This reactivity could in principle be more complicated than anticipated, since it has been reported that the reactivity of **1** with simple Pd(II) complexes such as $Li_2[PdCl_4]$[10] or $Pd(OAc)_2$[11,12] gives the

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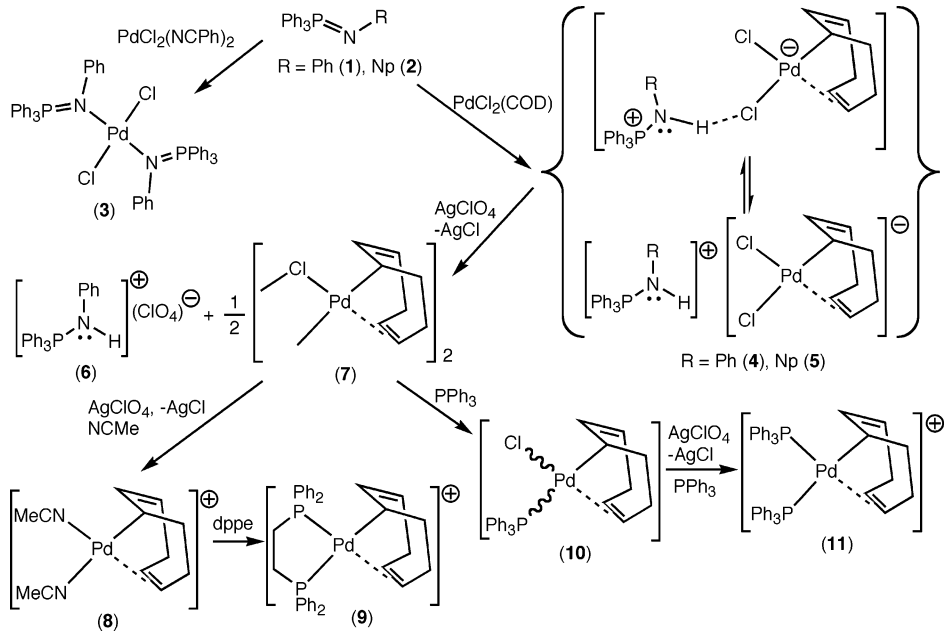
Scheme 1. Synthesis and Reactivity of Iminophosphoranes 1 and 2



cyclopalladated derivative $[Pd(\mu\text{-}Cl)\{C_6H_4(PPh_2{=}NPh)\text{-}2\}]_2$ through a C−H bond activation reaction.

Results and Discussion

The starting iminophosphoranes $Ph_3P{=}NR$ (R = Ph, **1**; Np, **2**) were prepared following published methods.[13] The reaction of phenylazide or 1-naphthylazide with PPh_3 (1:1 molar ratio) in dry CH_2Cl_2 gives **1** or **2**, respectively, isolated as white solids. Compound **1** reacts with $PdCl_2(NCPh)_2$ (2:1 molar ratio) in acetone to give **3** (Scheme 1), with two bonded iminophosphoranes **1**, according to its analytical and spectroscopic data. Thus, a simple ligand exchange reaction has occurred, instead of a nucleophilic attack on the nitrile ligand.[7] The IR spectrum of **3** shows the ν_{PN} stretch at 1313 cm^{-1}, shifted to low energy with respect to the free ligand **1** (1345 cm^{-1}) and strongly suggesting the N-bonding of **1**, while the trans arrangement of the chloride ligands can be inferred from the observation of a single band at 317 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum of **3** shows a single peak at $\delta = 30.06$ ppm, strongly deshielded with respect to the free ligand ($\delta = 3.38$ ppm) and also in good agreement with the N-coordination of **1**.

A quite different process has been observed in the reactivity of **1** or **2** with another Pd precursor. The reaction of $PdCl_2$-(COD) with **1** or **2** (1:1 molar ratio) in CH_2Cl_2 at 25 °C results in the clean synthesis of complex **4** or **5**, respectively (Scheme 1). The X-ray crystal structure of complex **4** has been determined by diffraction methods. Parameters concerning data collection and refinement are presented in Table 1, and selected bond lengths and angles are given in Table 2. The structure of **4** (Figure 1) shows that the complex possesses an anionic organometallic part (Figure 2) and a cationic organic part. The anionic organometallic part shows a Pd atom in a distorted square-planar environment, bonded to two cis chlorine ligands, Cl(1) and Cl(2), and to a disordered cyclooctadienyl ligand (ring C1A to C8A for one of the congeners in Figure 2; see SI for the other congener), meaning that the initial cyclooctadiene ligand has been deprotonated at a methylene group adjacent to an olefinic C=C bond. The organic fragment is an amino−phosphonium cation, showing that the initial iminophosphorane **1** has been protonated at the iminic atom N(1). The two fragments are in close contact, joined by a hydrogen bond between the NH group and the chlorine atom Cl(1).

The hydrogen bond is characterized by the intermolecular distances Cl(1)···H(1N) [2.3800 Å] and N(1)···Cl(1) [3.131(3) Å] and the angle N(1)−H(1N)···Cl(1) [143°]. These values fall at the low end of the usual range of distances found in the literature for similar hydrogen bonds.[14] Moreover, it must be taken into account that this type of hydrogen bonds has been described as robust and useful as structure-directing tools.[14c] In fact, the presence of this hydrogen bond in **4**—even in solution—is remarkable and has important consequences for its chemical behavior.

Concerning the cationic organic fragment, the P(1)−N(1) bond distance [1.624(3) Å] suggests a high degree of single-bond character since it is identical, within experimental error, to those found in $[Ph_3PN(H)Ph](BF_4)$ [1.621(4) and 1.635(4) Å],[15a] and it is longer than that found in the free iminophosphorane $Ph_3P{=}NPh$ [1.603(3) Å].[15b] On the other hand, the anionic organometallic fragment shows the Pd atom in a very distorted environment. The disordered cyclooctadienyl ligand is σ-bonded through the carbon atom C(5AB); there is a nonbonded olefinic group [C(6AB)−C(7A) in the congener shown in Figure 2] and a bonded olefinic fragment [C(1A)−C(2AB)]. The different Pd−C bond distances are almost identical, within experimental error, to those reported previously

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Table 1. Crystal Data and Structure Refinement for Compound 4·CH_2Cl_2

empirical formula	$C_{33}H_{34}Cl_4NPPd$
fw	723.80
temp (K)	150(1)
radiation (λ, Å)	0.71073
cryst syst	monoclinic
space group	*I*2/*a*
a (Å)	19.369(4)
b (Å)	12.150(2)
c (Å)	27.890(6)
β (deg)	103.74(3)
V (Å^3)	6376(2)
Z	8
D_{calc} (Mg/m^3)	1.508
μ (mm^{-1})	0.992
cryst size (mm^3)	0.12 × 0.27 × 0.32
no. of reflns collected	25 791
no. of indep reflns	7078 (R_{int} = 0.0316)
no. of data/restraints/params	7078/20/407
goodness-of-fit on F^2	1.064
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0403, wR2 = 0.1088
R indices (all data)	R1 = 0.0609, wR2 = 0.1149
largest diff peak, hole (e·Å^{-3})	0.878 and −1.259

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 4·CH_2Cl_2

Pd(1)−C(5AB)	2.029(4)	Pd(1)−C(1A)	2.171(9)
Pd(1)−C(2AB)	2.160(4)	Pd(1)−C(2B)	2.25(2)
Pd(1)−Cl(1)	2.4847(11)	Pd(1)−Cl(2)	2.3548(10)
C(5AB)−C(6AB)	1.497(6)	C(6AB)−C(7A)	1.292(9)
C(7A)−C(8A)	1.519(10)	C(8A)−C(1A)	1.419(12)
C(1A)−C(2AB)	1.327(10)	C(2AB)−C(3A)	1.605(9)
C(3A)−C(4A)	1.550(15)	C(4A)−C(5AB)	1.529(13)
P(1)−N(1)	1.624(3)	N(1)−C(9)	1.418(4)
C(5AB)−Pd(1)−C(1A)	91.5(3)	C(5AB)−Pd(1)−C(2AB)	84.08(19)
C(5AB)−Pd(1)−Cl(2)	90.21(14)	C(1A)−Pd(1)−Cl(2)	163.7(2)
C(2AB)−Pd(1)−Cl(2)	160.43(16)	C(5AB)−Pd(1)−Cl(1)	176.32(16)
C(1A)−Pd(1)−Cl(1)	86.1(5)	C(2AB)−Pd(1)−Cl(1)	92.56(13)
Cl(2)−Pd(1)−Cl(1)	93.38(4)	C(9)−N(1)−P(1)	126.1(2)

for the η^1-η^2-cyclooctadienyl ligand in a dinuclear complex.[16] The Pd(1)−Cl(1) bond distance [2.4847(11) Å] is longer than the Pd(1)−Cl(2) bond distance [2.3548(10) Å], reflecting the higher trans influence of the σ-allyl carbon atom, and both distances are in the usual range for this type of bond.[15c]

The characterization of **4** and **5** in solution provides additional information. The $^{31}P\{^1H\}$ NMR spectra of **4** and **5** show a single peak in each case in good agreement with the presence of a phosphonium unit. The ^1H NMR spectra of **4** and **5** show 10 well-defined peaks, spread in the 1−6 ppm region and assigned to the 11 protons of the cyclooctadienyl ligand. The well-resolved line shapes of these peaks are temperature independent and suggest a static behavior of the ligand on the NMR time scale. The most remarkable feature of each spectrum is a wide peak at 10.78 ppm (**4**) or 11.16 ppm (**5**), assigned to the NH proton. The shift of this peak to very low field suggests that the intermolecular hydrogen bond observed in the X-ray crystal structure of **4** is retained in solution. The $^{13}C\{^1H\}$ NMR spectra of **4** and **5** show all expected peaks for the structures shown in Scheme 1, and assignment of all signals in the ^1H and ^{13}C spectra was carried out with the help of homo- and heteronuclear correlation 2D spectra and selective 1D NOESY and ROESY.

While ^{31}P NMR data clearly show the presence of the aminophosphonium unit in solution, and ^1H NMR data suggest the perseverance of the hydrogen bond, also in solution, ^{13}C NMR data indicate that the allyl unit on the cyclooctadienyl ligand is η^1-σ bonded. The clear shielding of the coordinated C═C olefinic bond with respect to the free olefin and the appearance of the metalated Pd*C*H signal in the alkylic region are strong evidence for the η^1-allyl−η^2-olefin bonding mode of the cyclooctadienyl ligand.[16]

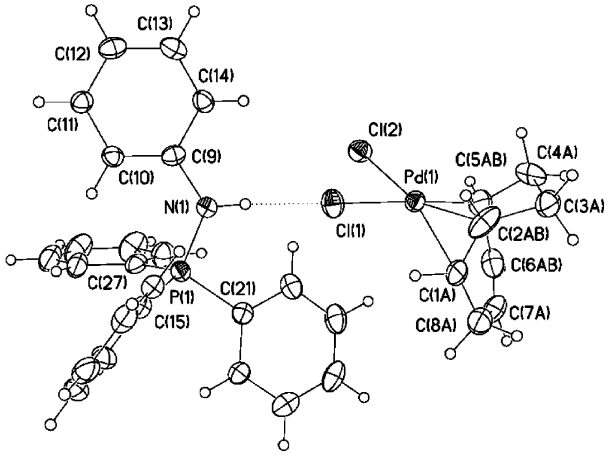

Figure 1. Thermal ellipsoid drawing of **4**·CH_2Cl_2 showing the hydrogen bond between cation and anion. Ellipsoids representing non-H atoms are drawn at 50% probability level.

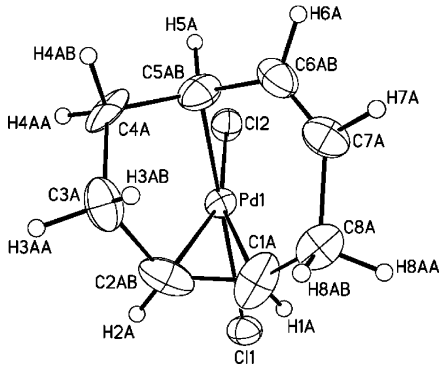

Figure 2. Thermal ellipsoid plot of one disordered anionic organometallic congener of **4**·CH_2Cl_2. Ellipsoids representing non-H atoms are drawn at 50% probability level.

Additional evidence for the presence of the hydrogen bond in solution is provided by the measurement of the molar conductance Λ_M of **4** in acetone.[17] It must be noted that the NMR spectra in acetone-d_6 show the same features as those obtained in $CDCl_3$ or CD_2Cl_2. The experimental value is Λ_M = 31.1 Ω^{-1} cm^2 mol^{-1}. Typical values of molar conductance for 1:1 electrolytes appear in the range 100−120 Ω^{-1} cm^2 mol^{-1},[17] so this result means that **4** is not completely dissociated and that the hydrogen bond is present to a significant extent in solution. However, the nonzero value of Λ_M also means that an equilibrium between the dissociated (ionic) and associated (neutral) forms must be operative in solution. This equilibrium seems to be shifted mainly to the associated neutral form due to the hydrogen bond and has to be very fast with respect to the NMR time scale since only one species is observed in solution.

The other singular fact about **4** and **5** is the generation of the cyclooctadienyl ligand from the coordinated 1,5-cyclooctadiene by deprotonation with an external base.[16] A plausible mechanism for this process is presented in Scheme 2 and could involve the exo nucleophilic attack of the iminophosphorane (through the iminic N atom) on one olefinic C═C bond, giving a σ-alkyl

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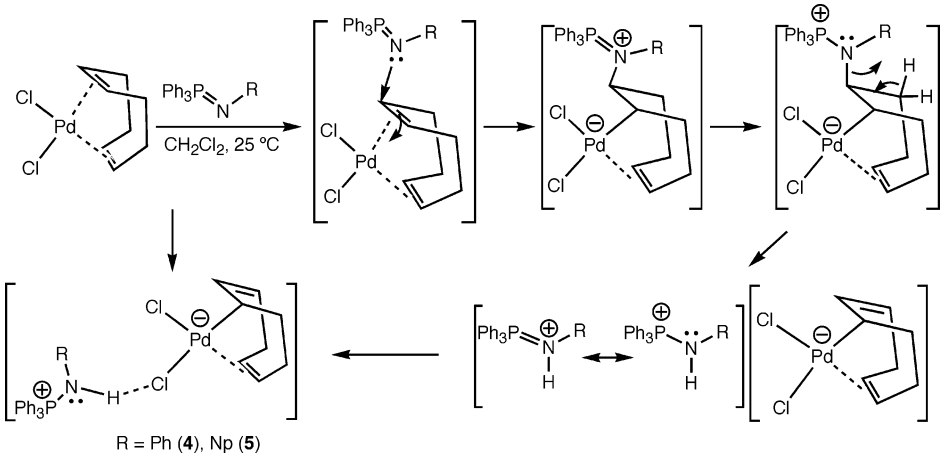
Scheme 2. Proposed Mechanism for Synthesis of 4 and 5



intermediate similar to those reported with phosphorus ylides.[4a,b] Once the C−N coupling has taken place, this intermediate could undergo intramolecular deprotonation on the methylene adjacent to the attack position, giving the amino−phosphonium unit and the dichloro η^1-η^2-cyclooctadienyl Pd(II) derivative. The formation of the intermolecular H bond could be the final step. This process is rather sensitive to the type of base. It has been reported[16] that the treatment of $PdCl_2$(COD) with NEt_3 gives complex **7**; that is, there is no interaction between the ammonium salt $[HNEt_3]^+$ and the cyclooctadienyl anionic complex, while reaction of $PdCl_2$(COD) with DBU (1,8-diazabicyclo-[5.4.0]undec-7-ene) results in the recovery of the starting compounds.

η^1-σ-Allyl ligands are very scarce, and the stability of this bonding mode in **4** and **5** is noteworthy.[18] We have probed the reactivity of **4** in order to test this stability and the possible interconversion into the more usual η^3-allyl bonding mode. First, we have transformed **4** (or **5**) into a more useful starting product.

The reaction of **4** with $AgClO_4$ (1:1 molar ratio) in MeOH gives the mixture of the amino−phosphonium salt **6**, the known organometallic **7**,[16] and AgCl. All components of this mixture could be isolated in pure form by adequate choice of solvents (see Experimental Section). Thus, the hydrogen bond in **4** is cleaved by the chloride abstraction and subsequent dimerization. The ^{1}H NMR spectrum shows the peak assigned to the NH proton at 8.06 ppm, upfield shifted from the starting product **4** (10.78 ppm) and as expected for the disappearance of the hydrogen bond. Complex **7** has already been reported,[16] and the method described here could be considered as a synthetic alternative. Moreover, **7** is a good starting compound for preparing other η^1-η^2-cyclooctadienyl complexes and also for checking the interconversion between the η^1- and η^3-bonding modes of the allyl fragment of the cyclooctadienyl ligand. In principle, the creation of empty coordination sites should provide a reasonable pathway to the η^1 to η^3 conversion.

Complex **7** reacts with $AgClO_4$ in NCMe to give the bis-solvate **8** (Scheme 1). The characterization of **8** shows that the cyclooctadienyl ligand retains its η^1-η^2-bonding mode. The IR spectrum, the elemental CHN analyses, and the ^{1}H NMR spectrum of **8** confirm the coordination of two molecules of NCMe to the Pd center. Attempts to use less coordinating ligands such as THF did not yield the final complexes as solids due to extensive decomposition. The NCMe ligands in **8** can be removed by reaction with other more coordinating groups. The reaction of **8** with dppe (1:1 molar ratio) in CH_2Cl_2 gives **9** (Scheme 1). The ^{31}P{^{1}H} NMR spectrum shows a low-field AB spin system (50.78 and 49.31 ppm, $^2J_{PP}$ = 37 Hz), due to the two P atoms of the dppe ligand bonded as a P,P′-chelate. Thus, **8** and **9** again present the cyclooctadienyl ligand with the η^1-η^2-bonding mode.

Complex **7** reacts with PPh_3 in CH_2Cl_2 (Scheme 1) to give **10** as a 1:1 mixture of geometric isomers after cleavage of the chlorine bridging system. Complex **10** has been characterized by the usual analytic and spectroscopic means (see Experimental Section), which confirm that the η^1-allyl coordination persists. Chloride abstraction on **10**, promoted by silver salts, in solvents with low bonding ability, might reasonably be expected to promote the $\eta^1-\eta^3$ interconversion of the allyl fragment. However, treatment of a solution of **10** in THF with $AgClO_4$ (1:1 molar ratio) gives a mixture of several products, as is clear from the ^{31}P{^{1}H} NMR spectrum of the crude solid. From this mixture one main component (ca. 50%) could be identified, the bis-phosphino derivative **11** (Scheme 1). Complex **11** can be independently prepared in pure form by reaction of **10** with $AgClO_4$ and PPh_3 (1:1:1 molar ratio), as shown in Scheme 1 and as described in the Experimental Section, and it is easily characterized due to the observation of an AB spin system (23.39 and 22.89 ppm, $^2J_{PP}$ = 43 Hz) in the ^{31}P{^{1}H} NMR spectrum, assigned to the two cis P atoms. We have not been able to determine the nature of the other species, although it seems that the presence of complex **11** in the mixture suggests that the hypothetical monophosphino-(η^1,η^3-cyclooctadienyl) complex is not stable and evolves with transfer of one PPh_3 ligand. All of these results, and especially the syntheses of **8**−**11**, indicate that the $\eta^1-\eta^3$ interconversion of the allyl fragment is not a favored process in this case and that the stable bonding form of the cyclooctadienyl ligand is the $\eta^1-\eta^2$ form, that is, acting as a three-electron donor ligand.

Conclusion

The reactivity of the iminophosphoranes Ph_3P═NPh and Ph_3P═N-1-Np (Ph = phenyl, Np = naphthyl) toward different palladium substrates gives different types of products. When $PdCl_2$(COD) is used as substrate, the iminophosphorane attacks one olefinic bond and the expected C−N coupling is produced, followed by deprotonation and formation of an organopalladium compound with the cyclooctadienyl ligand. The iminophosphorane is thus transformed into an amino−phosphonium salt, which forms a strong hydrogen bond [N−H···Cl−Pd] with a coordinated chlorine ligand. The cyclooctadienyl ligand is η^1-

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η^2 bonded, and the η^1 fragment belongs to an allylic group. This η^1 coordination of the allyl group has proved to be very stable, and all attempts to promote an $\eta^1-\eta^3$ interconversion of the allyl fragment were unsuccessful.

Experimental Section

Safety Note: *Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared, and they should be handled with great caution. See: *J. Chem. Educ.* **1973**, *50*, A335−A337.

General Methods. Solvents were dried and distilled under argon using standard procedures before use. Elemental analyses were carried out on a Perkin-Elmer 2400-B microanalyzer. Infrared spectra (4000−200 cm^{-1}) were recorded on a Perkin-Elmer 883 infrared spectrophotometer from Nujol mulls between polyethylene sheets. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded in $CDCl_3$, CD_2Cl_2, or acetone-d_6 solutions at 25 °C (other temperatures were specified) on Bruker AvanceII-300, Avance-400, and Avance-500 spectrometers (δ, ppm; J, Hz); ^1H and $^{13}C\{^1H\}$ were referenced using the solvent signal as internal standard, while $^{31}P\{^1H\}$ was referenced to H_3PO_4 (85%). The ^1H SELNO-1D, SELRO-1D, and NOESY-2D NMR experiments were performed with optimized mixing times (D8/P15), depending of the irradiated signal. ESI/APCI mass spectra were recorded using an Esquire 3000 ion-trap mass spectrometer (Bruker Daltonic GmbH, Bremen, Germany) equipped with a standard ESI/APCI source. Samples were introduced by direct infusion with a syringe pump. Nitrogen served both as the nebulizer gas and the dry gas. Helium served as a cooling gas for the ion trap and collision gas for MS^n experiments. Other mass spectra (positive ion FAB) were recorded from CH_2Cl_2 solutions on a V. G. Autospec spectrometer. Molar conductance measurements were carried out in acetone solutions ($c = 5 \times 10^{-4}$ M) on a Philips PW-9509 digital conductivity meter. The starting compounds $Ph_3P{=}NPh$ (**1**) and $Ph_3P{=}N$-1-Np (**2**) were prepared according to the Staudinger method by reaction of the corresponding azides with PPh_3.[13] Complexes $PdCl_2(NCPh)_2$[19] and $PdCl_2(COD)$[20] were also prepared by reported procedures.

Synthesis of 3. To a suspension of $PdCl_2(NCPh)_2$ (0.100 g, 0.26 mmol) in acetone (20 mL) was added **1** (0.184 g, 0.52 mmol). The resulting mixture was stirred at room temperature for 7 h. During the reaction time, the initial suspension gradually dissolved, giving a clear yellow solution. This solution was evaporated to small volume (2 mL) and treated with 20 mL of Et_2O, giving **3** as a yellow solid. Obtained: 0.12 g (52%). Anal. Calc for $C_{48}H_{40}Cl_2N_2P_2Pd$ (884.12): C, 65.21; H, 4.56; N, 3.17. Found: C, 64.90; H, 4.47; N, 3.10. MS (MALDI+): *m/z* 849 (100%) $[M - Cl]^+$. IR (ν, cm^{-1}): 1313 (ν_{PN}), 317 (ν_{PdCl}). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.06. ^1H NMR ($CDCl_3$): δ 6.62−6.67 (m, 3H, $H_o + H_p$, NPh), 7.00 (d, 2H, H_m, NPh, $^3J_{HH} = 7.1$), 7.29 (m, 6H, H_m, PPh_3), 7.42 (m, 3H, H_p, PPh_3), 7.82 (m, 6H, H_o, PPh_3).

Synthesis of 4. A solution of $PdCl_2(COD)$ (0.200 g, 0.70 mmol) in 20 mL of CH_2Cl_2 was added dropwise to a solution of **1** (0.247 g, 0.70 mmol) in 10 mL of CH_2Cl_2. The resulting yellow solution was stirred at 25 °C for 2 h. The solvent was then evaporated to dryness, and the residue was treated with 20 mL of Et_2O to give **4** as a yellow solid, which was filtered, washed with additional Et_2O (10 mL), and air-dried. Obtained: 0.273 g (61%). Anal. Calc for $C_{32}H_{32}Cl_2NPPd$ (638.9): C, 60.16; H, 5.05; N, 2.19. Found: C 60.18; H 5.03; N 2.31. MS (MALDI+): *m/z* 354 (100%) $[PhN(H){=}PPh_3]^+$. IR (ν, cm^{-1}): 1304 (ν_{PN}), 341, 321 (ν_{PdCl}). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 32.31. ^1H NMR ($CDCl_3$): δ 1.09 (m, 1H, CH_2, C_8H_{11}), 1.50 (m, 1H, CH_2, C_8H_{11}), 1.80−1.86 (m, 2H, CH_2, C_8H_{11}), 2.35 (m, 1H, CH_2, C_8H_{11}), 2.70 (td, 1H, CH_2, C_8H_{11}, $^2J_{HH} = 19.9$, $^3J_{HH} = 5.7$), 3.79 (m, 1H, H_1 (PdCH), C_8H_{11}), 4.99 (t, 1H, H_2, free =CH, C_8H_{11}, $^3J_{HH} = 8.7$), 5.66 (t, 1H, bonded =CH, C_8H_{11}, $^3J_{HH} = 7.7$), 5.78 (m, 1H, H_3, free =CH, C_8H_{11}), 6.32 (m, 1H, bonded =CH, C_8H_{11}), 6.90 (t, 1H, H_p, NPh, $^3J_{HH} = 7.5$), 7.01 (t, 2H, H_m, NPh, $^3J_{HH} = 7.5$), 7.10 (d, 2H, H_o, NPh), 7.56 (m, 6H, H_m, PPh_3), 7.68 (m, 3H, H_p, PPh_3), 7.78 (m, 6H, H_o, PPh_3), 10.78 (s, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.34 (CH_2, C_8H_{11}), 28.94 (CH_2, C_8H_{11}), 39.96 (CH_2, C_8H_{11}), 57.30 (C_1, PdCH, C_8H_{11}), 100.08 (bonded =CH, C_8H_{11}), 114.23 (bonded =CH, C_8H_{11}), 121.04 (d, C_i, PPh_3, $^1J_{PC} = 93.8$), 122.97 (d, C_o, NPh, $^3J_{PC} = 6.7$), 123.91 (C_p, NPh), 129.02 (C_m, NPh), 129.83 (d, C_m, PPh_3, $^3J_{PC} = 13.4$), 132.12 (C_2, free =CH, C_8H_{11}), 132.98 (C_3, free =CH, C_8H_{11}), 133.87 (d, C_o, PPh_3, $^2J_{PC} = 11.1$), 134.84 (d, C_p, PPh_3, $^4J_{PC} = 2.9$), 138.52 (d, C_i, NPh, $^2J_{PC} = 2.5$).

Synthesis of 5. Complex **5** was prepared following the same procedure as that reported for **4**. Thus, $PdCl_2(COD)$ (0.200 g, 0.70 mmol) was reacted with **2** (0.282 g, 0.70 mmol) in CH_2Cl_2 (30 mL) to give **5** as a yellow solid. Obtained: 0.29 g (60%). Anal. Calc for $C_{36}H_{34}Cl_2NPPd$ (688.96): C, 62.76; H, 4.97; N, 2.03. Found: C, 62.90; H, 5.35; N, 2.10. MS (MALDI+): *m/z* 404 $[C_{10}H_7N(H){=}PPh_3]^+$. IR ($\nu$, cm^{-1}): 1306 (ν_{PN}), 325, 297 (ν_{PdCl}). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 36.34. ^1H NMR ($CDCl_3$): δ 1.09 (m, 1H, CH_2, C_8H_{11}), 1.48 (m, 1H, CH_2, C_8H_{11}), 1.77−1.81 (m, 2H, CH_2, C_8H_{11}), 2.30 (m, 1H, CH_2, C_8H_{11}), 2.70 (m, 1H, CH_2, C_8H_{11}), 3.77 (m, 1H, H_1, PdCH, C_8H_{11}), 4.95 (m, 1H, H_2, free =CH, C_8H_{11}, $^3J_{HH} = 8.5$), 5.63 (t, 1H, bonded =CH, C_8H_{11}, $^3J_{HH} = 7.8$), 5.75 (m, 1H, H_3, free =CH, C_8H_{11}), 6.27 (m, 1H, bonded =CH, C_8H_{11}), 7.05−7.09 (m, 2H, $H_2 + H_3$, $C_{10}H_7$), 7.24−7.32 (m, 2H, $H_4 + H_6$, $C_{10}H_7$), 7.46 (m, 6H, H_m, PPh_3), 7.53 (d, 1H, H_5, $C_{10}H_7$, $^3J_{HH} = 7.7$), 7.58−7.64 (m, 4H, H_7, $C_{10}H_7 + H_p$, PPh_3), 7.75 (m, 6H, H_o, PPh_3), 8.15 (d, 1H, H_8, $C_{10}H_7$, $^3J_{HH} = 7.9$), 11.16 (s, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.07 (CH_2, C_8H_{11}), 28.85 (CH_2, C_8H_{11}), 39.83 (CH_2, C_8H_{11}), 57.77 (C_1, PdCH, C_8H_{11}), 99.83 (bonded =CH, C_8H_{11}), 101.30 (s, C_3, C_8H_{11}), 114.16 (bonded =CH, C_8H_{11}), 121.72 (d, C_i, PPh_3, $^1J_{PC} = 105.2$), 123.69 (d, C_8, $C_{10}H_7$, $^4J_{PC} = 0.7$), 124.92 (d, C_3, $C_{10}H_7$, $^4J_{PC} = 2.2$), 125.28 (d, C_2, $C_{10}H_7$, $^3J_{PC} = 8.1$), 126.27−126.48 (C_4, C_6, $C_{10}H_7$), 126.48 (C_5, $C_{10}H_7$), 127.72 (C_7, $C_{10}H_7$), 129.58 (d, C_m, PPh_3, $^3J_{PC} = 13.2$), 130.66 (C_2, C_8H_{11}), 131.57 (C_9, $C_{10}H_7$), 131.63 (C_{10}, $C_{10}H_7$), 133.97 (d, C_o, PPh_3, $^2J_{PC} = 11.02$), 134.26 (d, C_1, $^2J_{PC} = 0.7$), 134.58 (d, C_p, PPh_3, $^4J_{PC} = 2.9$).

Synthesis of 6 and 7. To a suspension of **4** (0.154 g, 0.24 mmol) in MeOH (15 mL) was added $AgClO_4$ (0.055 g, 0.26 mmol). The resulting mixture was stirred at 25 °C for 20 min with exclusion of light. After the reaction time, the gray suspension (which contains AgCl and complex **7**) was filtered through a Celite pad. (i) The resulting yellow solution was evaporated to small volume (∼2 mL). By Et_2O addition (15 mL) and further stirring **6** was obtained as a white solid. Obtained: 0.083 g (76%). (ii) The gray precipitate was suspended in 20 mL of CH_2Cl_2, extracted during 20 min at 25 °C and then filtered through a Celite pad. The resulting yellow solution was evaporated to dryness to obtain **7** as a yellow solid. Obtained: 0.025 g (21%). Complex **7** has been previously reported.[16] Characterization of **6**. Anal. Calc for $C_{24}H_{21}ClNO_4P{\cdot}0.8H_2O$ (468.3): C, 61.56; H, 4.86; N, 3.00. Found: C, 61.23; H, 4.70; N, 3.10. MS (MALDI+): *m/z* 354 (100) $[PhN(H){=}PPh_3]^+$. IR (ν, cm^{-1}): 1303 (ν_{PN}), 3147 (ν_{NH}). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 32.96$. ^1H NMR ($CDCl_3$): δ 7.00 (d, 2H, H_o, NPh, $^3J_{HH} = 7.8$), 7.03 (t, 1H, H_p, NPh, $^3J_{HH} = 7.8$), 7.15 (t, 2H, H_m, NPh), 7.68 (m, 6H, H_m, PPh_3), 7.80−7.84 (m, 9H, $H_p + H_o$, PPh_3), 8.06 (d, 1H, NH, $^2J_{PH} = 9.3$).

Synthesis of 8. $AgClO_4$ (0.245 g, 1.18 mmol) was added to a suspension of **7** (0.270 g, 0.54 mmol) in NCMe (10 mL), and the resulting mixture was stirred at room temperature for 20 min with exclusion of light. The gray suspension was then filtered through a Celite pad, and the resulting yellow solution was evaporated to small volume (∼1 mL). By Et_2O addition (20 mL) and further stirring, **8** was obtained as a yellow solid. Obtained: 0.214 g (67%).

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Anal. Calc for $C_{12}H_{17}ClN_2O_4Pd$ (395.15): C, 36.47; H, 4.34; N, 7.09. Found: C, 36.29; H, 4.04; N, 6.91. MS (MALDI+): *m/z* 396 $[M + H]^+$. IR (ν, cm^{-1}): 2350, 2319 (ν_{CN}). ^1H NMR ($CDCl_3$): δ 1.48 (m, 1H, CH_2, C_8H_{11}), 1.67 (m, 1H, CH_2, C_8H_{11}), 1.95−2.08 (m, 2H, CH_2, C_8H_{11}), 2.24 (s, br, 6H, NCMe), 2.27 (m, 1H, CH_2, C_8H_{11}), 2.78 (td, 1H, CH_2, C_8H_{11}, $^2J_{HH}$ = 18.7, $^3J_{HH}$ = 6.3), 4.22 (m, 1H, H_1, PdCH, C_8H_{11}), 4.96 (t, 1H, H_2, free =CH, C_8H_{11}, $^3J_{HH}$ = 8.3), 5.72 (m, 1H, bonded =CH, C_8H_{11}), 5.84 (td, 1H, H_3, free =CH, C_8H_{11}, $^3J_{HH}$ = 8.2, $^4J_{HH}$ = 3.8), 6.36 (m, 1H, bonded =CH, C_8H_{11}).

Synthesis of 9. 1,2-Bis(diphenylphosphino)ethane (0.198 g, 0.50 mmol) was added to a solution of **8** (0.196 g, 0.50 mmol) in CH_2Cl_2 (20 mL), and the resulting mixture was stirred for 1 h at 25 °C and then filtered through Celite. The obtained yellow solution was evaporated to dryness, and the residue treated with Et_2O (15 mL). Further stirring gave **9** as a white solid. Obtained: 0.201 g (56%). Complex **11** was recrystallized from CH_2Cl_2/hexane, giving colorless crystals of **11**·0.4CH_2Cl_2, which were used for analytic and spectroscopic purposes. The amount of CH_2Cl_2 was quoted by integration of the corresponding peak on the ^1H NMR spectrum. Anal. Calc for $C_{34}H_{35}ClO_4P_2Pd$·0.4CH_2Cl_2 (745.4): C, 55.43; H, 4.84. Found: C, 55.83; H, 5.05; MS (MALDI+): *m/z* 611 $[M - ClO_4]^+$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 49.31, 50.78 (AB spin system, 2PPh_2, $^2J_{PP}$ = 37.0). ^1H NMR ($CDCl_3$): δ 1.62 (m, 1H, CH_2, C_8H_{11}), 1.90 (m, 2H, CH_2, C_8H_{11}), 2.35 (m, 3H, CH_2, C_8H_{11}), 2.54 (m, 2H, CH_2, dppe), 2.96 (m, 2H, CH_2, dppe), 4.95 (m, 1H, H_1, PdCH, C_8H_{11}), 5.18 (t, 1H, H_2, free =CH, C_8H_{11}, $^3J_{HH}$ = 9.3), 5.27 (m, 1H, bonded =CH, C_8H_{11}), 5.54 (m, 1H, H_3, free =CH, C_8H_{11}), 5.72 (m, 1H, bonded =CH, C_8H_{11}), 7.44−7.59 (m, 20H, PPh_2, dppe).

Synthesis of 10. To a solution of **7** (0.220 g, 0.44 mmol) in CH_2Cl_2 (20 mL) was added PPh_3 (0.230 g, 0.88 mmol). The resulting solution was stirred at room temperature for 30 min, then evaporated to dryness. The oily residue was treated with Et_2O (15 mL), giving **10** as a yellow solid. Obtained: 0.170 g (75%). Complex **10** was characterized as a equimolecular mixture of cis and trans isomers. Complex **10** was recrystallized from CH_2Cl_2/Et_2O, giving yellow crystals of **10**·0.5CH_2Cl_2, which were used for analytic and spectroscopic purposes. Anal. Calc for $C_{26}H_{26}ClPPd$·0.5 CH_2Cl_2 (553.8): C, 57.47; H, 4.91. Found: C, 57.01; H, 4.85. MS (MALDI+): *m/z* 476 $[M - Cl]^+$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.52 (s, PPh_3), 24.81(s, PPh_3) (cis/trans mixture). ^1H NMR ($CDCl_3$): δ 1.51 (m, CH_2, C_8H_{11}), 1.59 (m, CH_2, C_8H_{11}), 1.64 (m, CH_2, C_8H_{11}), 1.71 (m, CH_2, C_8H_{11}) 1.83−2.30 (m, CH_2, C_8H_{11}), 2.55−2.73 (m, 2H, CH_2, C_8H_{11}), 2.81 (m, CH_2, C_8H_{11}), 3.09 (m, CH_2, C_8H_{11}), 3.80 (m, PdCH, C_8H_{11}), 4.15 (m, PdCH, C_8H_{11}), 5.05−5.17 (m, H_2, free =CH, C_8H_{11}, both isomers), 5.43 (t, bonded =CH, C_8H_{11}, $^3J_{HH}$ = 7.5), 5.50 (t, bonded =CH, C_8H_{11}, $^3J_{HH}$ = 6.0), 5.57 (m, H_3, free =CH, C_8H_{11}), 5.67 (m, H_3, free =CH, C_8H_{11}), 5.78 (m, bonded =CH, C_8H_{11}), 6.05 (m, bonded =CH, C_8H_{11}), 7.40−7.43 (m, $H_m + H_p$, PPh_3, both isomers), 7.62−7.71 (m, H_o, PPh_3, both isomers).

Synthesis of 11. To a solution of **10** (0.076 g, 0.15 mmol) in THF (20 mL) were added $AgClO_4$ (0.031 g, 0.15 mmol) and PPh_3 (0.039 g, 0.15 mmol). The resulting mixture was stirred at room temperature for 20 min with exclusion of light. After the reaction time, the gray suspension was filtered through a Celite pad, and the resulting solution was evaporated to small volume (~2 mL). By Et_2O addition (15 mL) and stirring **11** was obtained as a yellow solid. Obtained: 0.070 g (56%). Anal. Calc for $C_{44}H_{41}ClO_4P_2Pd$ (837.6): C, 63.09; H, 4.93. Found: C, 62.98; H, 5.00. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.39, 22.89 (AB spin system, $^2J_{PP}$ = 43.0). ^1H NMR ($CDCl_3$): δ 1.25−1.38 (m, 2H, CH_2, C_8H_{11}), 1.84−2.04 (m, 3H, CH_2, C_8H_{11}), 2.16 (m, 1H, CH_2, C_8H_{11}), 5.16−5.27 (m, 2H, $H_3 + H_2$, free =CH, C_8H_{11}), 5.31−5.34 (m, 2H, PdCH + bonded =CH, C_8H_{11}), 5.87 (t, 1H, bonded =CH, C_8H_{11}, $^3J_{HH}$ = 8.7), 7.24−7.42 (m, 30H, PPh_3).

Crystal Structure Determination and Data Collection for 4·CH_2Cl_2. Crystals of **4**·CH_2Cl_2 of adequate quality for X-ray measurements were grown by vapor diffusion of Et_2O into a CH_2Cl_2 solution of **4** at −5 °C. A single crystal was mounted at the end of a quartz fiber in a random orientation, covered with perfluorinated oil, and placed under a cold stream of nitrogen gas. Data collection was performed at 150 K on an Oxford Diffraction Xcalibur2 diffractometer using graphite-monocromated Mo Kα radiation (λ = 0.71073 Å). A hemisphere of data was collected based on ω-scan and ϕ-scan series. The frames were integrated using the program CrysAlis RED,[21] and the integrated intensities were corrected for absorption with SADABS.[22]

Structure Solution and Refinement. The structure was solved and developed by Patterson and Fourier methods.[23] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed at idealized positions and treated as riding atoms. Each hydrogen atom was assigned an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of its parent atom. The structures were refined to F_o^2, and all reflections were used in the least-squares calculations.[24] The anionic complex centered on Pd1 has two major groups for one disorder assembly: the organic ligand. The olefin is η^2 bonded to Pd1 and the allyl function is η^1 ligated. The ring runs in opposite directions in the two disorder groups (see SI). The two disorder groups are labeled "A" and "B", and the atoms common to the two are labeled "AB". The atomic sites for the first disordered congener, "A", beginning with the olefinic group, are [olefinic:] C1A, C2AB, [methylene:] C3A, C4A, [allyl:] C5AB, C6AB, C7A, [methylene:] C8A. The second congener, in the same order of chemical entities as that used for the first disorder group, consists of [olefinic:] C2AB, C2B, [methylene:] C3B, C6AB, [allyl:] C5AB, C6B, C7B, [methylene:] C8B we report the structure in space group *I*2/*a*. The structure can also be set on a monoclinic C-centered lattice, with space group *C*2/*c*. This would require the use of a nonreduced net in the *ac*-plane. In order to reduce correlations in the refinement, we used the "most reduced" cell, the one with the shortest available axes, which is also the least oblique cell choice, which in this case corresponds to *I*2/*a*. The dimensions of the C-centered cell are *a* = 30.053 Å, *b* = 12.150 Å, *c* = 19.369 Å, β = 115.23°.

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Supporting Information Available: Tables giving complete data collection parameters, atomic coordinates, bond distances and angles, and thermal parameters for **4**·CH_2Cl_2. This material is available free of charge via the Internet at http://pubs.acs.org

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