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Parent-amido (NH_2) palladium(II) complexes: Synthesis, reactions, and catalytic hydroamination☆

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The treatment of $[PdL_3(NH_3)](OTf)_n$ ($n = 1$; $L_3 = (PEt_3)_2(Ph)$, $(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)$, $n = 2$; $L_3 = (dppe)(NH_3)$) with $NaNH_2$ in tetrahydrofuran at ambient temperature or −78 °C afforded the dimeric and monomeric parent-amido palladium(II) complexes *anti*-$[Pd(PEt_3)(Ph)(\mu\text{-}NH_2)]_2$ (**1**), $[Pd(dppe)(\mu\text{-}NH_2)]_2(OTf)_2$ (**2**), and $Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(NH_2)$ (**3**), respectively. The molecular structures of the amido-bridged (μ-NH_2) dimeric complexes **1** and **2** were determined by single-crystal X-ray crystallography. The monomeric amido complex **3** reacted with trace amounts of water to give a hydroxo complex, $Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(OH)$ (**4**). Exposing complex **3** to an excess of water resulted in the complete conversion of the complex into two species $[Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(OH_2)]^+$ and $[Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(NH_3)]^+$. Complex **3** reacted with diphenyliodonium triflate ($[Ph_2I]OTf$) to give the aniline complex $[Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(NH_2Ph)]OTf$. The reaction of **3** with phenylacetylene ($HC{\equiv}CPh$) yielded a palladium(II) acetylenide $Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(C{\equiv}CPh)$ (**5**), quantitatively, along with the liberation of ammonia. The reaction of **3** with dialkyl acetylenedicarboxylate yielded diastereospecific palladium(II) vinyl derivatives (*Z*)-$Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(CR{=}CR(NH_2))$ ($R = CO_2Me$ (**6a**), CO_2Et (**6b**)). The reaction of complexes **6a** and **6b** with *p*-nitrophenol produced $Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(OC_6H_4\text{-}p\text{-}NO_2)$ (**7**) and *cis*-$CHR{=}CR(NH_2)$, exclusively. Reactions of **3** with either dialkyl maleate (*cis*-$(CO_2R)CH{=}CH(CO_2R)$) ($R = CH_3, CH_2CH_3$) or *cis*-stilbene (*cis*-$CHPh{=}CHPh$) did not result in any addition product. Instead, isomerization of the *cis*-isomers to the *trans*-isomers occurred in the presence of catalytic amounts of **3**. Complex **3** reacted with a stoichiometric amount of acrylonitrile (CH_2CHCN) to generate a metastable insertion product, $Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(CH(CN)CH_2NH_2)$. On the other hand, the reaction of **3** with an excess of acrylonitrile slowly produced polymeric species of acrylonitrile. The catalytic hydroamination of olefins with NH_3 was examined in the presence of $Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(OTf)$, producing a range of hydroaminated products of primary, secondary, and tertiary amines with different molar ratios of more than 99% overall yield. A mechanistic feature for the observed catalytic hydroamination is described with regard to the aminated derivatives of palladium(II).

1. Introduction

The amido complexes of late transition metals have attracted considerable interest because of their potential involvement as intermediates in metal-catalyzed carbon–nitrogen bond formation [1,2]. Recent studies on

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the chemistry of these complexes have focused mostly on arylamido complexes, in which the metal-amido bond may be stabilized by partial delocalization of the electron density on the amido nitrogen to an aryl substituent [2]. On the other hand, complexes with a parent-amido ligand (NH_2) have attracted less attention [1,3–5]. Despite this, such species are important as feasible intermediates in metal-catalyzed amination reactions with ammonia [6]. Furthermore, considering the importance of palladium as a primary metal used in homogeneous catalysis, it is essential to develop the chemistry with this metal [6a,7].

Monomeric amido complexes have strong affinity to undergo substitutional dimerization or oligomerization, yielding amido-bridged species, which are particularly crucial for coordinatively unsaturated complexes. Therefore, a common synthetic strategy for preparing monomeric metal amides is to use a sterically hindered ancillary ligand, such as bulky tertiary phosphines and chelates including pincer-type ligands, to avoid substitutional dimerization [5–7]. An earlier report on the synthesis and thermal stability of a dimethylamido palladium(II), Pd(2,6-(Ph_2PCH_2)$_2C_6H_3$)(NMe_2), showed that the monomeric amido complex with a terdentate PCP pincer is resistant to β-hydrogen elimination and thermal decomposition at low temperatures of less than −10 °C [8a]. A previous study on the regiospecific reactivity of an arylamido platinum(II) containing the same pincer Pt(2,6-(Ph_2PCH_2)$_2C_6H_3$)(NH(Tol-*p*)) toward the C=C bond of acrylonitrile to yield the addition product of aminoalkyl complex, Pt(2,6-(Ph_2PCH_2)$_2C_6H_3$)(CH(CN)CH_2NH(Tol-*p*)) provided a mechanistic information on one of the key steps in the catalytic hydroamination of acrylonitrile with NH_2(Tol-*p*) [8b].

This article reports on a series of dimeric and monomeric parent-amido (NH_2) complexes of palladium(II) with an ancillary ligand framework of a different coordination mode as part of an ongoing study of the stability and reactivity of the parent-amido complexes. In the present study for the synthesis of a monomeric parent-amido palladium(II) complex, a sterically hindered cyclohexyl derivative of PCP pincer was used to preclude substitutional dimerization. The title complex exhibited unique reactivity toward activated olefins and acetylenes to produce regio- and diastereospecific aminated derivatives of palladium(II), respectively, via nucleophilic attack of the coordinated NH_2.

In this study, the catalytic hydroamination of olefins with ammonia in the presence of the relevant title complex was also examined. The mechanistic feature of the catalytic hydroamination is discussed in regard to the probed reaction profiles in palladium(II) aminated derivatives.

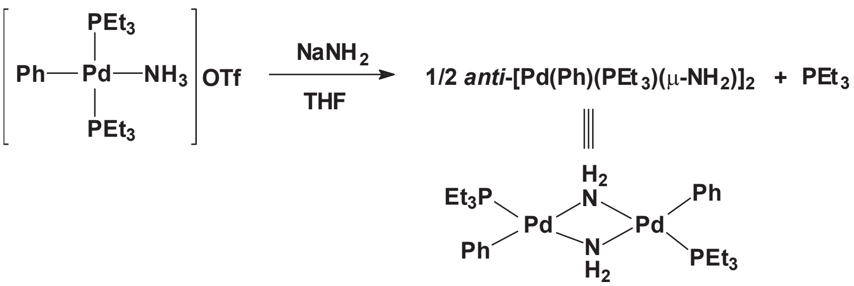
2. Results and discussion

2.1. NH_2-bridged dimeric complexes

2.1.1. *anti*-[Pd(PEt_3)(Ph)(μ-NH_2)]$_2$ (**1**) and [Pd(dppe)(NH_2)]$_2$(OTf)$_2$ (**2**)

The reaction of a tetrahydrofuran (THF) solution of *trans*-[Pd(PEt_3)$_2$(Ph)(NH_3)]OTf with $NaNH_2$ at ambient temperature produced a gray suspension containing a single compound of palladium(II) along with dissociated triethylphosphine, as evidenced by the $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 1). A pure off-white palladium(II) dimer *anti*-[Pd(PEt_3)(Ph)(μ-NH_2)]$_2$ (**1**) was obtained from an *n*-pentane extract of the residues resulting from the reaction mixture. The $^{31}P\{^1H\}$ NMR spectrum of complex **1** in d_6-benzene showed a single peak at δ 20.2, which is indicative of a single compound in solution. In the $^{13}C\{^1H\}$ NMR spectrum, the methylene carbon attached directly to the phosphorus resonates at δ 15.61 (^1J(CP) = 26.7 Hz) as a doublet. In the ^1H NMR spectrum, the bridged-amide protons (μ-NH_2) were observed at δ −1.35 as a broad signal.

Attempts to prepare a parent-amido complex with a chelate ligand dppe under similar reaction conditions as for complex **1** were unsuccessful. The reaction of [Pd(dppe)(NH_3)$_2$](OTf)$_2$ with $NaNH_2$ in THF at ambient temperature resulted in a deep red solution containing a palladium(0) complex Pd(dppe), which was trapped in situ by treatment with dimethyl acetylenedicarboxylate (dmad) to yield Pd(dppe)(dmad), as verified by the $^{31}P\{^1H\}$ NMR spectrum, showing a single resonance at δ 48.0 in d_6-benzene [9]. The formation of Pd(dppe) from the reaction is likely a consequence of the feasible generation of a monomeric bis(amido) species Pd(dppe)(NH_2)$_2$, which undergoes facile reductive elimination by releasing hydrazine (N_2H_4), although electron transfer from a base (NH_2^-) cannot be excluded. Previous studies showed that hydrazine formation from the oxidation of coordinated ammonia to a diruthenium complex [10] or from adsorbed NH_2 species on transition metal surfaces [11] is feasible. On



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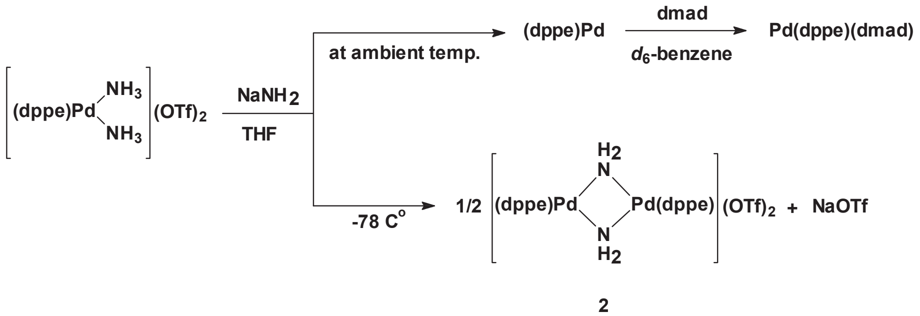
Scheme 1. Synthesis of *anti*-[Pd(PEt_3)(Ph)(μ-NH_2)]$_2$ (**1**).



Scheme 2. Synthesis of $[Pd(dppe)(\mu\text{-}NH_2)]_2(OTf)_2$ (**2**).

the basis of the above result, the reaction was performed at low temperatures. The reaction of $[Pd(dppe)(NH_3)_2](OTf)_2$ with $NaNH_2$ in THF at −78 °C (dry ice/acetone) afforded a dicationic amido-bridged dimeric complex $[Pd(dppe)(\mu\text{-}NH_2)]_2(OTf)_2$ (**2**) in 67% isolated yield (Scheme 2). The ^1H and $^{31}P\{^1H\}$ NMR spectra of **2** in $CDCl_3$ exhibit an upfield broad signal at δ −0.19 corresponding to bridged-amide protons (μ-N*H*$_2$) and a single ^{31}P resonance at δ 53.2, respectively. The counter anion $CF_3SO_3^-$ can be established by the $\nu(SO_3)$ at 1154 and 1266 cm^{-1} in the IR and the $^{19}F\{^1H\}$ NMR resonance at δ −78.9. The molar conductivity measurement for **2** in nitromethane reveals that the complex is a 1:2 electrolyte (Λ_M = 184 Ω^{-1} cm^2 mol^{-1}, [**2**] = 0.50 × 10^{-3} M). The microanalytical data for **1** and **2** are consistent with the dimeric formulation (see Section 4).

*2.1.2. Molecular structures of anti-[Pd(PEt$_3$)(Ph)(μ-NH$_2$)]$_2$ (**1**) and [Pd(dppe)(μ-NH$_2$)]$_2$(OTf)$_2$ (**2**)*

The molecular structures of **1** and **2** were determined by single-crystal X-ray crystallography (Figs. 1 and 2). Single crystals suitable for X-ray crystallography were grown either by the slow evaporation of an *n*-hexane solution of **1** or by the slow diffusion of a mixture of diethyl ether and *n*-pentane (1:1) into a dichloromethane solution of **2**. Both complexes **1** and **2** crystallize in the monoclinic space group $P2_1/n$. For **1**, there are two crystallographically independent but chemically identical molecules. The two independent molecular structures of **1** contain the respective Pd_2N_2 rings puckered with the dihedral angles of 53.1(2)° and 55.2(2)°. The Pd–Pd distances are 2.9594(10) and 2.9401(9) Å, respectively. The cation of complex **2** contains a puckered Pd_2N_2 ring with a dihedral angle of 28.8(0.15)°, which is smaller than that of **1**. Therefore, the Pd–Pd distance 3.0669(8) Å in **2** is slightly larger. The observed Pd–Pd distances for **1** and **2** indicate that there is no bonding between Pd and Pd [12], which are comparable to the Pt–Pt distances in the range of 3.087–3.134 Å, observed in the NH_2-bridged platinum(II) dimers, *anti*-$[Pt(POPh_2)(PMePh_2)(\mu\text{-}NH_2)]_2$ [4b], $[Pt(PMe_2Ph)_2(\mu\text{-}NH_2)]_2^{2+}$ [4c], and *anti*-$[PtMe(PPh_3)(\mu\text{-}NH_2)]_2$ [5a]. The

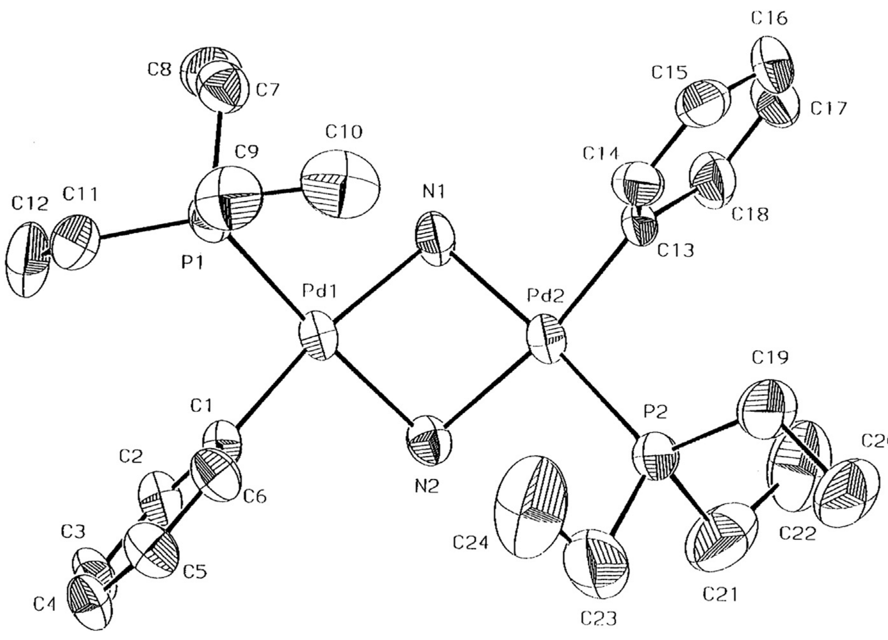


Fig. 1. The molecular structure for one of the two crystallographically independent molecules of **1** shown with 40% thermal ellipsoids. For clarity hydrogen atoms have been omitted.

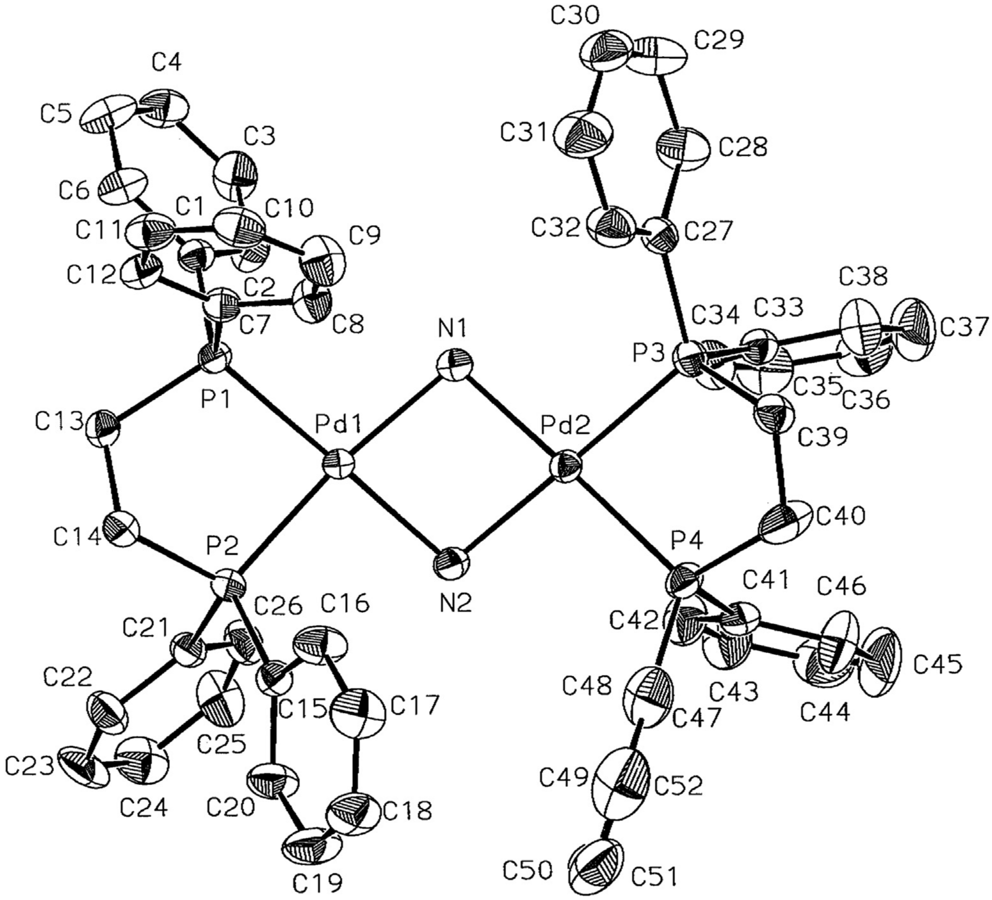


Fig. 2. The structure of the cation of **2** shown with 40% thermal ellipsoids. The counter anions $2[CF_3SO_3]^-$ and hydrogen atoms were omitted for clarity.

Pd–N bond lengths for **1** and **2** are in the range of 2.067(7)–2.127(7) Å. For the angles within the bridge about palladium and nitrogen, the respective Pd–N–Pd and N–Pd–N bond angles are 88.8(3)–90.4(3)° and 77.7(3)–78.3(3)° for **1** and 95.0(2)–95.6(2)° and 79.2(2)–79.6(2)° for **2**. The selected bond lengths (in angstroms) and angles (in degrees) for complexes **1** and **2** are given in Tables 1 and 2, respectively. For reference, all the X-ray crystallographic data of **1** and **2** are provided in Supplementary Data, including the crystal data, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters.

The amido-bridged dimeric complexes **1** and **2** in the solid state and in solution are stable in air for a period of days. No reactions with unsaturated molecules, such as CO_2, CH_2=CHCN, dimethyl acetylenedicarboxylate, diethyl maleate, and cyclohexene were observed, indicating a lack of nucleophilicity of the bridging NH_2. Considering the observed stability, it is unanticipated that although the few analogous platinum(II) dimers have been reported [4,5a], the title complexes are, to the best of our knowledge, the first structurally determined NH_2-bridged palladium(II) dimers [13].

*2.2. Monomeric amido complex Pd(2,6-($Cy_2PCH_2)_2C_6H_3$)(NH_2) (**3**) and its reactivity*

Because the formation of amido-bridged dimeric species resulted from substitutional dimerization, a palladium(II) ammine complex containing a *trans*-spanning terdentate ligand was as a synthetic precursor for the preparation of a monomeric parent-amido palladium(II) complex. In a similar synthetic manner, as for **1**, treatment of the cationic ammine complex [Pd(2,6-($Cy_2PCH_2)_2C_6H_3$)(NH_3)](OTf) with $NaNH_2$ afforded the

Table 1
Selected bond lengths (Å) and angles (°) for one of the two crystallographically independent molecules of **1**.

Pd(1)–N(1)	2.104(7)	Pd(1)–C(1)	2.000(9)
Pd(1)–N(2)	2.085(7)	Pd(2)–C(13)	1.998(9)
Pd(2)–N(1)	2.067(7)	Pd(1)–P(1)	2.233(3)
Pd(2)–N(2)	2.127(7)	Pd(2)–P(2)	2.235(3)
Pd(2)–N(1)–Pd(1)	90.4(3)	N(2)–Pd(1)–P(1)	174.3(2)
Pd(1)–N(2)–Pd(2)	89.3(3)	N(1)–Pd(1)–P(1)	99.5(2)
N(2)–Pd(1)–N(1)	77.8(3)	C(13)–Pd(2)–N(1)	92.8(3)
N(1)–Pd(2)–N(2)	77.7(3)	C(13)–Pd(2)–N(2)	170.4(3)
C(1)–Pd(1)–N(2)	93.5(3)	C(13)–Pd(2)–P(2)	91.7(3)
C(1)–Pd(1)–N(1)	171.3(3)	N(1)–Pd(2)–P(2)	175.1(2)
C(1)–Pd(1)–P(1)	89.0(3)	N(2)–Pd(2)–P(2)	97.7(2)

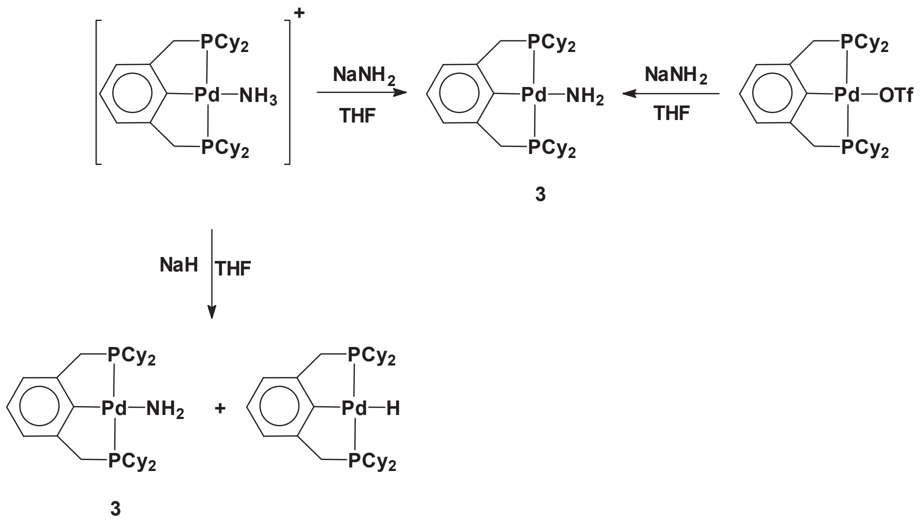
Table 2
Selected bond lengths (Å) and angles (°) for **2**.

Pd(1)–N(1)	2.089(6)	Pd(1)–P(1)	2.255(2)
Pd(1)–N(2)	2.067(6)	Pd(1)–P(2)	2.240(2)
Pd(2)–N(1)	2.069(6)	Pd(2)–P(3)	2.240(2)
Pd(2)–N(2)	2.075(6)	Pd(2)–P(4)	2.244(2)
Pd(2)–N(1)–Pd(1)	95.0(2)	N(1)–Pd(1)–P(1)	101.3(2)
Pd(1)–N(2)–Pd(2)	95.6(2)	P(2)–Pd(1)–P(1)	85.69(7)
N(2)–Pd(1)–N(1)	79.6(2)	N(1)–Pd(2)–P(3)	98.8(2)
N(1)–Pd(2)–N(2)	79.9(2)	N(2)–Pd(2)–P(3)	174.6(2)
N(2)–Pd(1)–P(2)	93.4(2)	N(1)–Pd(2)–P(4)	176.9(2)
N(1)–Pd(1)–P(2)	173.0(2)	N(2)–Pd(2)–P(4)	98.1(2)
N(2)–Pd(1)–P(1)	179.1(2)	P(3)–Pd(2)–P(4)	83.03(8)

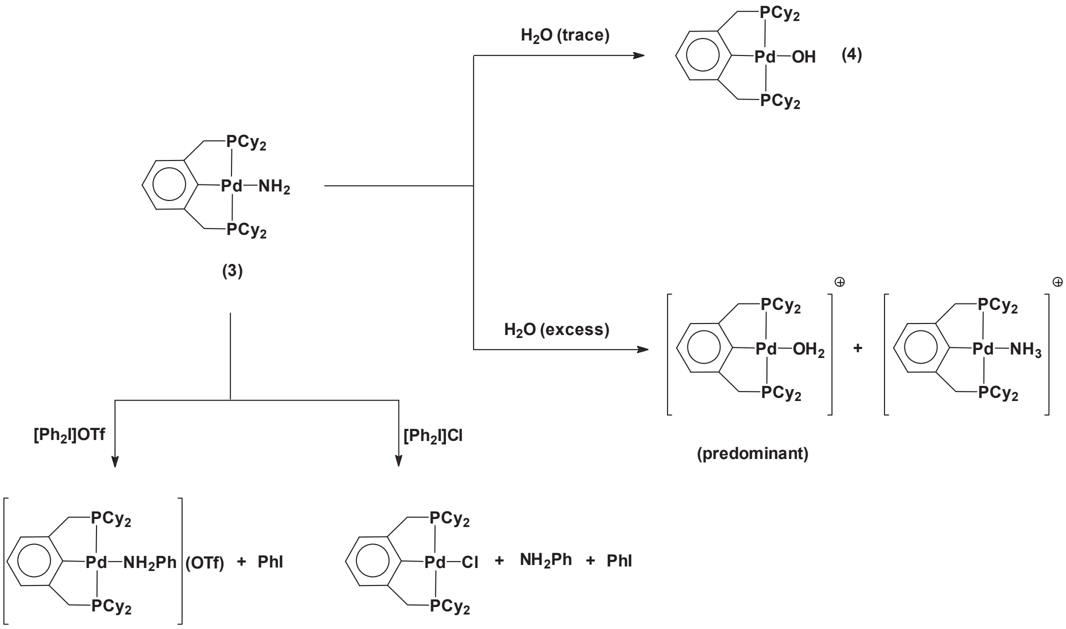
monomeric palladium(II) amide Pd(2,6-$(Cy_2PCH_2)_2C_6H_3$)(NH_2) (**3**). When NaH was used as a deprotonating agent in place of $NaNH_2$, the reaction yielded a mixture of two products, including mainly complex **3** along with a small amount of palladium(II) hydride (2,6-$(Cy_2PCH_2)_2C_6H_3$)PdH. The formation of the palladium(II) hydride was verified by the observation of upfield hydride resonance at δ −3.73 (t, ^2J(PH) = 16 Hz) in the ^1H NMR spectrum [8a,14]. On the other hand, the metathetical replacement of the triflate ligand in Pd(2,6-$(Cy_2PCH_2)_2C_6H_3$)(OTf) with $NaNH_2$ yielded the monomeric palladium(II) amide, exclusively. Scheme 3 represents the used synthetic routes. The formation of Pd(2,6-$(Cy_2PCH_2)_2C_6H_3$)(NH_2) (**3**) was established by the upfield shift of NH_2 resonance at δ −0.20 and the relative intensity of the methylene protons in the pincer ligand and NH_2 resonances in the ^1H NMR spectrum. On diluting a d_6-benzene solution of **3**, the NH_2 resonance shifts upfield, implicating intermolecular hydrogen bonding in the complexes.

Complex **3** is highly sensitive to air and moisture. The monomeric amido complex slowly (over the course of days) reacts with trace amounts of water to yield a hydroxo complex Pd(2,6-$(Cy_2PCH_2)_2C_6H_3$)(OH) (**4**) (Scheme 4). The hydroxo complex can be verified by the observation of upfield triplet resonance for the coordinated hydroxide (Pd–O*H*) at δ −1.22 with the small value of ^3J(PH) = 3.3 Hz in the ^1H NMR spectrum along with a single ^{31}P NMR resonance at δ 48.7 [15,16]. For further characterization, the hydroxo complex Pd(2,6-$(Cy_2PCH_2)_2C_6H_3$)(OH) was prepared independently by metathesis from Pd(2,6-$(Cy_2PCH_2)_2C_6H_3$)(OTf) and KOH in THF (see Section 4). The observed σ-ligand exchange reaction of **3** with H_2O compares well with a previous report on the reactivity of a parent-amido Ni(II) complex toward H_2O [17]. Exposing the complex **3** to an excess of water resulted in the immediate conversion of the complex into two species, which exhibit ^{31}P NMR resonance at δ 52.7 and δ 54.7 (predominant), respectively. The former is assigned to the cationic ammine species [Pd(2,6-$(Cy_2PCH_2)_2C_6H_3$)(NH_3)]$^+$, which was established by the observation of an identical $^{31}P\{^1H\}$ NMR resonance with the complex [Pd(2,6-$(Cy_2PCH_2)_2C_6H_3$)(NH_3)](OTf). The latter can be attributed to the cationic aqua complex [Pd(2,6-$(Cy_2PCH_2)_2C_6H_3$)(OH_2)]$^+$, as evidenced by the identical $^{31}P\{^1H\}$ NMR resonance at δ 54.7 with a complex prepared from Pd(2,6-$(Cy_2PCH_2)_2C_6H_3$)(BF_4) and H_2O in d_6-benzene. No formation of the hydroxo complex was observed from the reaction of **3** with an excess of water. Therefore, the observed results can be explained by a sequence of reactions involving the σ-ligand exchange of the amido complex with H_2O to give the hydroxo complex, which then protonates from excess water molecules to generate the observed cationic aqua complex (Scheme 4). The formation of a small amount of cationic ammine complex can be attributed to the ligand substitution of the cationic aqua complex with the liberated NH_3.

A d_6-benzene solution of **3** reacted with diphenyliodonium triflate ([Ph_2I]OTf) to give an *N*-phenylated amine complex [Pd(2,6-$(Cy_2PCH_2)_2C_6H_3$)(NH_2Ph)]OTf (Scheme 4). The formation of the cationic aniline complex was confirmed by its independent preparation from a reaction of Pd(2,6-$(Cy_2PCH_2)_2C_6H_3$)(OTf) with NH_2Ph in d_6-benzene (see Section 4). The reaction of a d_6-benzene solution of Pd(2,6-$(Cy_2PCH_2)_2C_6H_3$)(OTf) with NH_2Ph produced



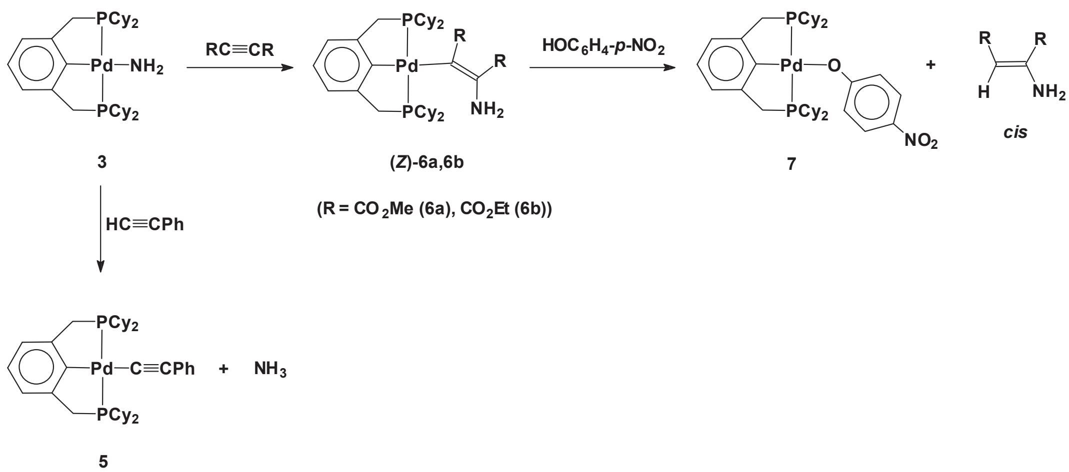
Scheme 3. Synthesis of Pd(2,6-$(Cy_2PCH_2)_2C_6H_3$)(NH_2) (**3**).



Scheme 4. Reactions of **3** with H_2O and $[Ph_2I]X$ (X = OTf, Cl).

$[Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(NH_2Ph)]OTf$, displaying a rather broad single $^{31}P\{^1H\}$ NMR resonance at δ 52.1 in accordance with that of the species generated by the reaction of **3** with $[Ph_2I]OTf$. An attempt to isolate the cationic aniline species was unsuccessful because of dissociation of the coordinated aniline, converting to $Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(OTf)$. In the meanwhile, reaction of **3** with the chloride salt of $[Ph_2I]Cl$ generated $Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)Cl$ along with the released NH_2Ph, which was identified by GC–MS (NH_2Ph: m/z = 93, 66, 39).

The amido complex **3** reacted readily with phenylacetylene (HC≡CPh) to quantitatively yield a palladium(II) acetylenide $Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(C{\equiv}CPh)$ (**5**) along with the liberation of ammonia, which was detected in the ^1H NMR spectrum (broad 1:1:1 triplet, at δ −0.15, $^1J(NH)$ = 41 Hz) (Scheme 5) [17]. Complex **5** was prepared from preparative scale experiment and fully characterized (see Section 4). Complex **5** shows its characteristic absorption peak for the $\nu(C{\equiv}C)$ at 2096 cm^{-1} in the IR spectrum, and the $^{13}C\{^1H\}$ NMR resonances for the coordinated acetylenide at δ 113.1 (t, Pd–*C*≡C, $^2J(CP)$ = 12 Hz) and at δ 118.3 (Pd–C≡*C*). These spectroscopic data are in good agreement with those reported for *trans*-$Pd(PEt_3)_2(C_6H_4\text{–}Me\text{-}p)(C{\equiv}CPh)$ at 2092 cm^{-1} in the IR, and at δ 119.8 (t, Pd–*C*≡C, $^2J(CP)$ = 20 Hz) and at δ 111.3 (Pd–C≡*C*) in the $^{13}C\{^1H\}$ NMR spectrum [18]. The observed reactivity for **3** toward phenylacetylene reveals that the coordinated NH_2 is highly basic for the complex to undergo σ-ligand exchange via protonation rather than the migratory insertion of the C≡C triple bond into the Pd–NH_2 via



Scheme 5. Reactions of **3** with RC≡CR (R = CO_2Me, CO_2Et) and HC≡CPh.

nucleophilic attack on the sp-carbon of HC≡CPh. In view of the thermodynamic aspect, the driving force for the formation of the palladium(II) acetylenide parallels the relative ground state stability in the order of M-C(sp) > M-$NH_2(sp^3)$ or M-C(sp^2, vinylic) [19,20].

Complex **3** undergoes clean reactions with activated acetylenes, such as dialkyl acetylenedicarboxylate (RC≡CR; R = CO_2Me, CO_2Et), to produce the diastereospecific insertion derivatives of Pd(2,6-$(Cy_2PCH_2)_2C_6H_3$)(CR=CR(NH_2)) (R = CO_2Me (**6a**), CO_2Et (**6b**)) (Scheme 5). Complexes **6a** and **6b** have been fully characterized by multinuclear NMR (^{1}H, ^{13}C, and ^{31}P) and fast atom bombardment mass spectrometry (FABMS). The formation of aminovinylic complexes was verified readily by the observation of resonances for the corresponding two methyl and two ethyl groups for the moiety of Pd(CR=CR(NH_2)) (R = CO_2Me, CO_2Et) in the ^{1}H and ^{13}C{^{1}H} NMR spectra. The amino protons (NH_2) resonate around δ 3.9 as a broad peak, which was confirmed by the D_2O exchange experiment. In the ^{1}H NMR spectra, the virtual triplet methylene protons (PCH_2) in the PCP pincer ligand were observed to be diastereotopic at δ 3.1 and 3.3 as a doublet of triplet ($^2J(H_aH_b)$ = 17.6 Hz, |^2J(PH) + ^4J(PH)| ≅ 8 Hz), respectively. In solution, no coordination of the amino group in the complex was observed, as evidenced by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy; all signals were intact on the addition of coordinating molecules, such as pyridine and PPh_3, to the d_6-benzene solution of **6a** and **6b**. Endeavors to isolate complexes **6a** and **6b** from solution were futile because of the high solubility in most organic solvents including *n*-pentane. Therefore, the removal of all volatiles from solution under high vacuum resulted in yellow solids, which afforded satisfactory FABMS data, displaying a parent molecular ion peak in good accordance with the calculated molecular weight in addition to the expected peaks because of molecular fragmentation. Although the absolute diastereomeric configuration of **6a** and **6b** could not be determined because of the failure to obtain suitable single crystals for an X-ray structural study, the stereochemistry of complexes **6a** and **6b** (*Z*)-isomer was assigned by performing subsequent reactions. A further reaction of **6a** and **6b** with an acidic phenol HOC_6H_4-*p*-NO_2 produced only a single isomeric product *cis*-CHR=CR(NH_2) (R = CO_2Me, CO_2Et) with the retention of the configuration, along with the palladium(II) *p*-nitrophenoxide Pd(2,6-$(Cy_2PCH_2)_2C_6H_3$)(OC_6H_4-*p*-NO_2) (**7**) (Scheme 5). The formation of Pd(2,6-$(Cy_2PCH_2)_2C_6H_3$)(OC_6H_4-*p*-NO_2) (**7**) was verified by its independent synthesis from the reaction of Pd(2,6-$(Cy_2PCH_2)_2C_6H_3$)(OTf) and Na(OC_6H_4-*p*-NO_2) in THF (see Section 4). As a control, reaction of a d_6-benzene solution of dialkyl acetylenedicarboxylate with gaseous ammonia produces an isomeric mixture of *cis*- and *trans*-(CHR=CR(NH_2)). The diastereoselective formation of (*Z*)-Pd(2,6-$(Cy_2PCH_2)_2C_6H_3$)(CR=CR(NH_2)) (**6a**, **6b**) resulting from the reaction of Pd(2,6-$(Cy_2PCH_2)_2C_6H_3$)(NH_2) (**3**) and RC≡CR implies that the insertion reaction presumably involves a concerted pathway, apparently excluding dissociative nucleophilic addition. The observed reactivity for the palladium(II) aminovinylic complexes toward HOC_6H_4-*p*-NO_2 in the ligand exchange reaction reveals that the σ-vinylic ligand is more basic than the σ-phenoxide, liberating stereoselective olefinic derivatives with retention of configuration. In view of the importance of using ammonia as a building block for the production of nitrogen-containing compounds [6], this study on the reaction profile of the *syn*-insertion of activated acetylene into the Pd–NH_2 bond in the title complex is noteworthy. Prior examples of the *syn*-insertion of alkynes and alkenes into the Pd–N bonds have rarely been found in arylamido complexes [21].

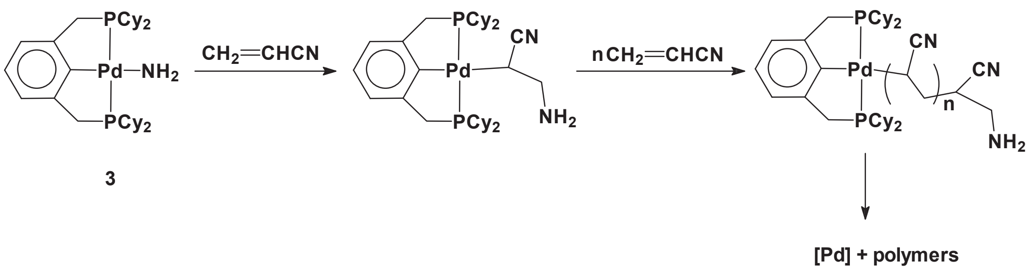
The insertion reaction of the C=C bond of dialkyl maleate (*cis*-(CO_2R)CH=CH(CO_2R)) (R = CH_3, CH_2CH_3) into the Pd–NH_2 bond of complex **3** was attempted, resulting in no formation of the insertion derivatives. Instead, dialkyl maleate isomerizes into dialkyl fumarate (*trans*-(CO_2R)CH=CH(CO_2R)) in the presence of a catalytic amount of **3**, as evidenced by ^{1}H NMR spectroscopy. The reaction proceeds rather slowly at ambient temperature, resulting in an isomeric *trans*/*cis* ratio of 0.8 (for 4 h) and 8.9 (for 24 h) for the dimethyl derivative (CO_2Me)CH=CH(CO_2Me). The conversion of dialkyl maleate (*cis*-isomer) into dialkyl fumarate (*trans*-isomer) was completed over a period of 5 days at ambient temperature. Similarly, a reaction of the parent-amido complex **3** with *cis*-stilbene (*cis*-CHPh=CHPh) was attempted, resulting in no reaction at ambient temperature. On the other hand, at an increased temperature of 50 °C, the complex **3** catalyzed the isomerization of *cis*-stilbene to *trans*-stilbene, resulting in a *trans*/*cis* ratio of 2.0 for 2 h. No insertion product was observed in the course of the catalytic isomerization. Isomerization did not occur in the absence of the parent-amido complex. As a control, no isomerization was observed in the reaction via a base, such as NH_3 or *p*-toluidine. The migratory insertion of the *cis*-isomers into the Pd–NH_2 bond followed by deinsertion cannot lead to the formation of *trans*-isomers because rotation of the C–C single bond in the insertion species *erythro*-Pd($CHXCHXNH_2$) cannot invert the configuration of the β-carbon atom. Therefore, the observed diastereomeric isomerization catalyzed by complex **3** can most likely be explained by a sequence of reactions as follows. Migratory insertion of the C=C bond of the *cis*-isomers into the Pd–NH_2 bond leads to a transient aminoalkyl species *erythro*-Pd($CHXCHXNH_2$), which undergoes β-H elimination to generate a Pd(II)-hydride and *cis*-CHX=$CXNH_2$. The Pd(II)-hydride reacts with *cis*-CHX=$CXNH_2$ with the opposite regiochemistry to generate Pd(C(NH_2)XCH_2X), in which the rotation of the C–C bond followed by elimination of the other β-H leads to the generation of a Pd(II)-hydride again along with *trans*-CHX=$CXNH_2$. The Pd(II)-hydride reacts with *trans*-CHX=$CXNH_2$ to afford *threo*-Pd($CHXCHXNH_2$), from which the isomerized *trans*-olefin can be released via deinsertion to regenerate complex **3**. A previous theoretical study demonstrated that β-H elimination from the ammonioalkyl complexes of group 10 metals is kinetically competitive in the catalytic hydroamination of ethylene with ammonia [22].

A stoichiometric reaction of **3** with acrylonitrile (CH_2CHCN) generated a metastable insertion product, Pd(2,6-$(Cy_2PCH_2)_2C_6H_3$)(CH(CN)CH_2NH_2), which was detected by ^{1}H and ^{31}P NMR spectroscopy (Scheme 6). A d_6-benzene solution of the reaction mixture showed anticipating proton resonances for the methyne (C*H*) and methylene (CH_2) protons of the Pd–CH(CN)CH_2NH_2 moiety around at

δ 2.2, 3.1, and 3.5 as multiplets in the ^1H NMR spectrum and a new single resonance at δ 49.0 in the $^{31}P\{^1H\}$ NMR spectrum. The observed proton resonances of the $Pd(CH(CN)CH_2NH_2)$ moiety are in good agreement with those of the analogous aminoalkyl platinum(II) complex, $Pt(2,6\text{-}(Ph_2PCH_2)_2C_6H_3)(CH(CN)CH_2NHTol\text{-}p)$ at δ 2.75 (m, 1H, C*H*), 3.08 (m, 1H, CH_a), and 3.45 (m, 1H, CH_b), respectively [8b]. Attempts to isolate the insertion product from the solution were unsuccessful because of decomposition to a couple of unidentified species. The reaction of **3** with an excess of acrylonitrile slowly produced polymeric species of acrylonitrile at ambient temperature, which precipitated in solution. The ^{31}P NMR resonance at δ 49.0 because of an aminoalkyl palladium(II) derivative observed at an early stage of the reaction mostly disappeared to generate a couple of new ^{31}P NMR resonances, one at δ 59.2 corresponding to a cationic acrylonitrile complex $[Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(CH_2{=}CHCN)]^+$ (vide infra, catalytic hydroamination of olefins with ammonia). The isolated polymer from the reaction mixture shows the characteristic absorption peaks for the $\nu(CN)$ at 2245 and 2204 cm^{-1} and for the $\nu(NH_2)$ at 3300 and 3360 cm^{-1} in the IR spectrum. As a control, the reaction of $Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(OTf)$ with an excess acrylonitrile generated $[Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(CH_2{=}CHCN)](OTf)$ without producing any polymeric species. Therefore, the observed results can be explained by a sequence of reactions involving migratory insertion of the C=C bond of acrylonitrile into the $Pd{-}NH_2$ bond at an early stages of the reaction to generate a metastable aminoalkyl palladium(II) complex, which undergoes the consecutive insertion of acrylonitrile into the Pd–C bond followed by the liberation of polymeric species (Scheme 6). The present result is comparable to a previous study on an aminoalkyl platinum(II) complex, which exhibited no further reactivity toward acrylonitrile, and is in line with the migratory insertion barriers for the σ-alkyl complexes in the order Pd(II) < Pt(II) [23]. Attempted reactions of **3** with unactivated olefins, such as 1-hexene, cyclohexene, and styrene, were futile presumably because of the insufficient nucleophilicity of the coordinated amide along with the rigidity of the sterically hindered pincer ligand in the title complex.

2.3. Catalytic hydroamination of olefins with ammonia

The catalytic hydroamination of various olefins with NH_3 was examined in the presence of $Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(OTf)$. Unless otherwise noted, the catalytic reactions were typically performed at a fixed concentration of olefin substrates (100 equiv) with various concentrations of NH_3 in the presence of a catalyst (1.0 equiv) for 12 h at 60 °C. The results are summarized in Table 3. For the catalytic hydroamination of acrylonitrile ($CH(CN){=}CH_2$) with NH_3 (entries 1–5), a range of hydroaminated products of primary ($CH_2(CN)CH_2NH_2$), secondary ($(CH_2(CN)CH_2)_2NH$), and tertiary ($(CH_2(CN)CH_2)_3N$) amines with different molar ratios were produced in an overall yield of more than 99%, indicating that the produced amine derivatives compete with ammonia as nucleophilic substrates. The catalytic overall yield increased considerably with increasing concentration of NH_3 (entries 2–5). The mole percent ratios of the produced amine derivatives (primary/secondary) generally increased with increasing concentration of ammonia (entries 3–5). On the other hand, at a relatively low concentration of ammonia compared to acrylonitrile (NH_3/acrylonitrile = 4/5), the tertiary amine derivative ($(CH_2(CN)CH_2)_3N$, 11 mol %) was produced along with the predominant formation of secondary amine ($(CH_2(CN)CH_2)_2NH$, 57 mol %) (entry 2). Hydroaminated products were not produced at a significantly low ratio of ammonia-to-acrylonitrile (NH_3/acrylonitrile = 1/5, entry 1). For the hydroamination of methyl acrylate ($CH_2{=}CHCO_2Me$) with ammonia, the reaction rate considerably decreased in comparison with those from acrylonitrile with ammonia, resulting in an overall yield of 47% at 80 °C for 18 days (entry 6). The resulting products were only a mixture of the secondary ($(CH_2(CO_2CH_3)CH_2)_2NH$, 83 mol %) and the tertiary ($(CH_2(CO_2CH_3)CH_2)_3N$, 17 mol %) amines without the primary amine ($CH_2(CO_2CH_3)CH_2NH_2$), apparently revealing that the generated primary amine (more basic than NH_3) subsequently attacks methyl acrylate to produce the secondary amine predominantly. For the hydroamination of crotononitrile (MeCH=CHCN, a mixture of *cis*- and *trans*-isomer with a ratio of ca. 1.0) with ammonia (entries 7–9), the reaction rate was much slower than that from acrylonitrile (or methyl acrylate) with ammonia. On the other hand, the resulting product was exclusively the primary amine ($CH_2(CN)CH(CH_3)NH_2$). No formation of the secondary and tertiary amines from the catalytic reaction can be attributable mostly to the steric effect of the produced primary amine. The catalytic hydroamination of other unsaturated hydrocarbons, such as cyclohexene, styrene, 1-hexene, 1-hexyne, and diphenylacetylene, with ammonia was attempted without success.



Scheme 6. Reaction of **3** with acrylonitrile.

Table 3
Hydroamination of olefins with NH_3 catalyzed by $Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(OTf)$.[a]

$$n\,CHR{=}CHX + NH_3 \xrightarrow[\text{benzene}]{[Pd]\ (1.0\ mol\%)} (CH_2X{-}CHR)_n(NH_{3-n}) \quad (R = H, Me;\ X = CN, C(O)OMe)$$

$$n = 1, 2, 3,$$

Entry	Olefin	NH_3 (molar equiv[b] or atm)	Overall yield (%)[c]	HA products (mol %)[c]		
				$n = 1$	$n = 2$	$n = 3$
1	$CH_2{=}CHCN$	20[d]	0[e]			
2	$CH_2{=}CHCN$	80[d]	12	32	57	11
3	$CH_2{=}CHCN$	100[d]	17	21	79	0
4	$CH_2{=}CHCN$	120[d]	20	29	71	0
5	$CH_2{=}CHCN$	7 atm[f]	>99	84	15	0
6	$CH_2{=}CHCO_2Me$	100[d]	47[g]	0	83	17
7	$MeCH{=}CHCN$[h]	300[d]	11[i]	100	0	0
8	$MeCH{=}CHCN$	7 atm[f]	9	100	0	0
9	$MeCH{=}CHCN$	25 atm[f]	29	100	0	0

[a] Reaction conditions: $Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(OTf)$ (3.0 mg, 4.0×10^{-3} mmol), [olefin] = 100 × [Pd].
[b] Molar equivalent to [Pd].
[c] ^1H NMR integration or GC-based yield for 12 h at 60 °C, unless otherwise noted. The overall yield is relative to the olefin.
[d] In a vacuum NMR tube.
[e] For 24 h.
[f] In a high pressure reactor.
[g] For 18 days at 80 °C.
[h] 150 equiv.
[i] For 4.5 days.

For a mechanistic feature, further experiments were conducted by NMR spectroscopy. The ^1H NMR spectrum of a $CDCl_3$ solution of $Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(OTf)$ in the presence of acrylonitrile with a slight excess displayed broad resonances at ambient temperature. The variable temperature experiments for the ^1H NMR spectra of the $CDCl_3$ solution revealed a dynamic process attributable to the rapid ligand exchange between the triflate and acrylonitrile in the complex (Fig. 3). The rate of exchange process is fast on the NMR time scale at >10 °C and decreases at low temperatures. The proton resonances for the coordinated acrylonitrile cleanly resolved at −22 °C, indicating the formation of a stable olefinic complex in solution. On the other hand, on the addition of a large excess amount of acrylonitrile (ca. 30 equiv) into the solution, the proton resonances for the free acrylonitrile displayed well-resolved sharp peaks at ambient temperature. The $^{31}P\{^1H\}$ NMR spectrum of this solution exhibited a sharp single resonance at δ 59.4, which is assignable to the cationic acrylonitrile complex $[Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(CH_2{=}CHCN)](OTf)$ analogous to the reported platinum(II) complexes [8b]. Attempts to isolate the olefinic complex from the solution were unsuccessful because of conversion into the palladium triflate $Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(OTf)$. The resulting cationic olefin complex is stable in solution in the presence of excess acrylonitrile for a period of several days at ambient or increased temperature (60 °C) without producing polymeric species or any other side products. The addition of NH_3 (excess) to this solution, however, immediately generated the cationic ammine complex $[Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(NH_3)](OTf)$ along with the acrylonitrile complex. Subsequently, the reaction mixture slowly undergoes a catalytic reaction to produce a mixture of hydroaminated products. No polymeric species was produced from the catalytic reaction.

In the catalytic reaction, a mechanism involving the coordination of ammonia to a palladium(II) sphere followed by deprotonation to generate a parent-amido complex can be excluded because polymeric species, which could be derived from a migratory insertion derivative of palladium(II), that is, an aminoalkyl complex, was not formed from the catalytic reaction (vide supra). A further experiment to examine the ability of ammonia to deprotonate the coordinated ammonia in $[Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(NH_3)](OTf)$ was conducted. The treatment of the amido complex **3** with NH_4OTf in d_6-benzene produced $[Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(NH_3)](OTf)$ and NH_3, quantitatively, as evidenced by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, apparently excluding the involvement of a Pd(II) amido species in the catalytic reaction. Therefore, the present catalytic reaction may proceed via the nucleophilic attack of ammonia on the precoordinated olefin to palladium(II) to generate a transient alkylammonium complex $[Pd(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(CH_2(CN)CH_2NH_3)]^+$ in parallel to a previous report on catalytic hydroamination by platinum(II) catalysts [8b]. A high concentration of ammonia would act as a base to transfer a proton from the suggested species to produce hydroaminated products (pathway A in Scheme 7). The relative stabilities of the σ-donor amine versus the π-olefinic acrylonitrile complexes showed that acrylonitrile practically competes with amine in the coordination spheres of palladium(II) [24] and platinum(II) [8b,25]. The nucleophilic addition of amines on the coordinated olefin to palladium(II) complexes has been well recognized [26]. An alternative pathway for the catalytic reaction likely involves a 5-coordinate Pd(IV)-hydride species, from

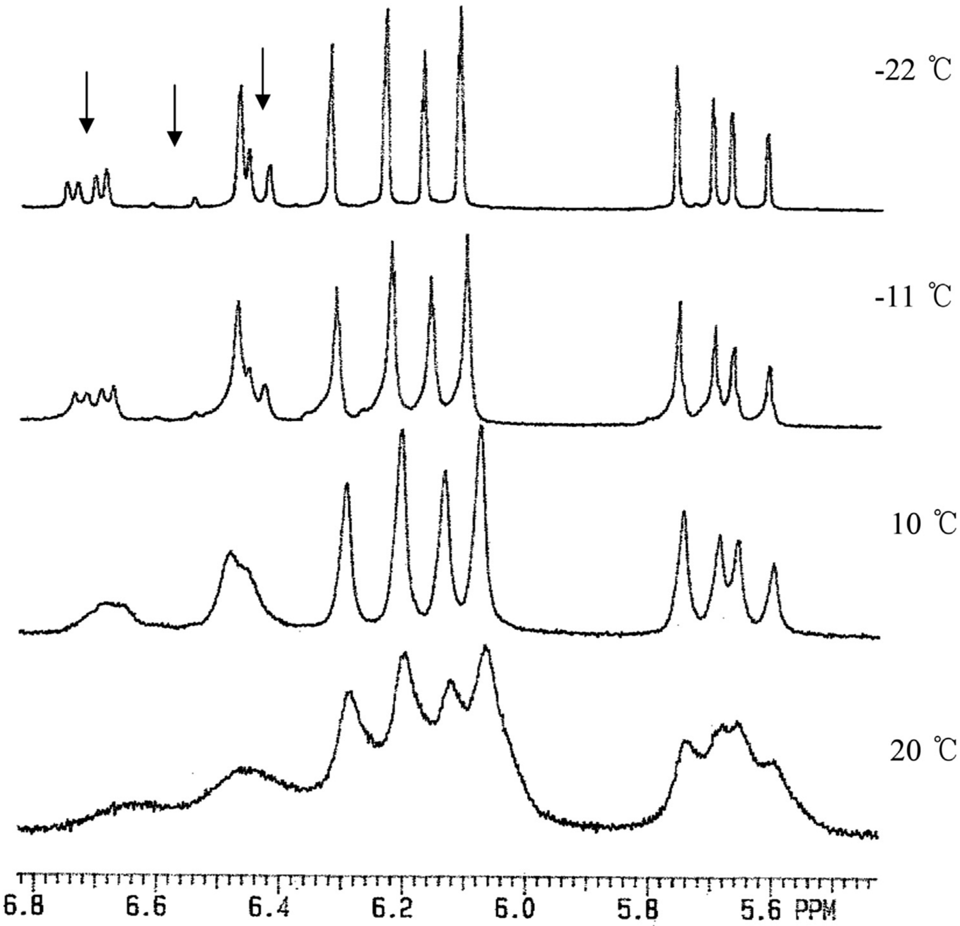


Fig. 3. The VT ^{1}H NMR spectra of $Pd(2,6-(Cy_2PCH_2)_2C_6H_3)(OTf)$ in the presence of $CH_2{=}CHCN$ in $CDCl_3$ show that there is a fast ligand exchange between the triflate and acrylonitrile in the complex on the NMR time scale at >10 °C. The resonances of the coordinated acrylonitrile resolve at −22 °C, being marked with arrows.

which C—H reductive elimination leads to hydroaminated products (pathway B in Scheme 7). Previous computational studies of the hydroamination of ethylene with ammonia or aniline catalyzed by d^8-metal complexes illustrated that intramolecular transfer of an alkylammonium proton to the metal center to generate a 5-coordinate (16-electron) metal-hydride intermediate is energetically feasible [22,27]. Scheme 7 presents plausible reaction pathways for the observed catalytic hydroamination of olefins with ammonia in the presence of the title complex.

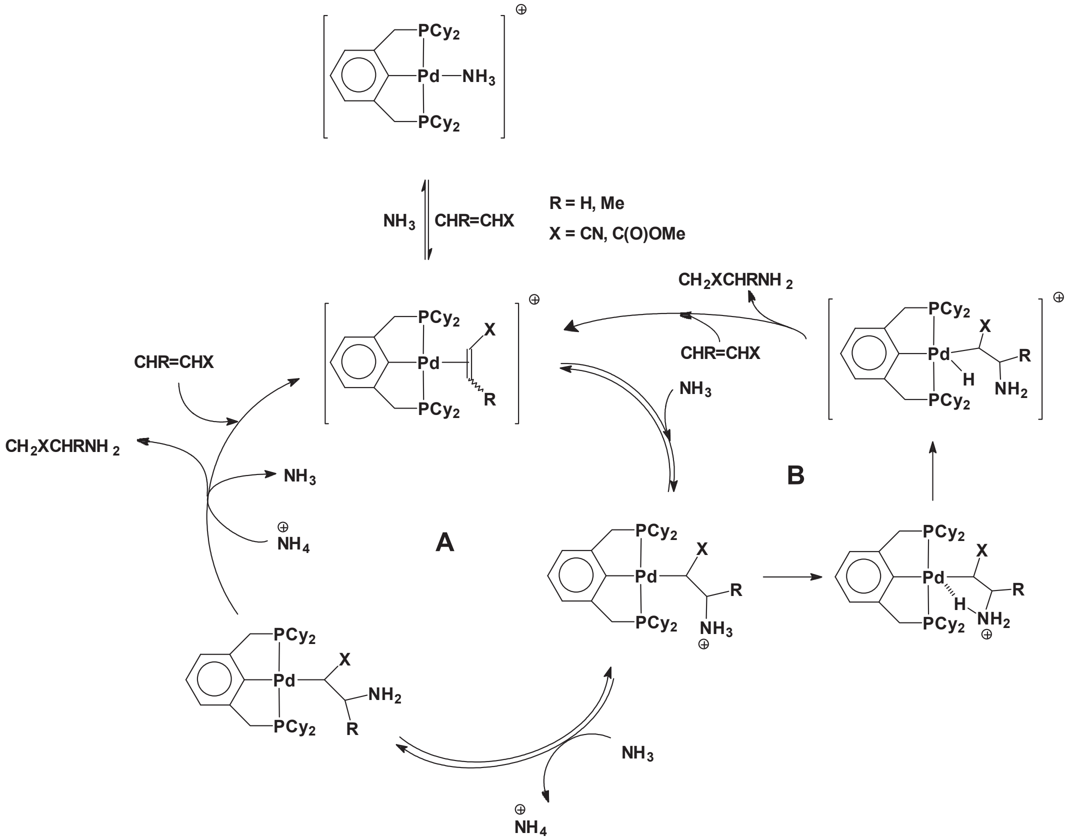
3. Summary

Novel parent-amido complexes of palladium(II) *anti*-$[Pd(PEt_3)(Ph)(\mu\text{-}NH_2)]_2$, $[Pd(dppe)(\mu\text{-}NH_2)]_2(OTf)_2$, and $Pd(2,6-(Cy_2PCH_2)_2C_6H_3)(NH_2)$ were prepared from the respective ammine complexes by deprotonation of the coordinated ammonia. The amido-bridged dimeric complexes are inert to unsaturated molecules, such as CO_2, activated olefins, and acetylenes, revealing a lack of nucleophilicity of the bridging NH_2. The monomeric parent-amido complex $Pd(2,6-(Cy_2PCH_2)_2C_6H_3)(NH_2)$ showed the strong nucleophilicity of the coordinated amide toward a range of electrophiles to undergo σ-ligand exchange or addition reactions with activated acetylenes and olefins to yield diastereo- and regiospecific aminated derivatives of palladium(II) complexes. The palladium(II) triflate $Pd(2,6-(Cy_2PCH_2)_2C_6H_3)(OTf)$ catalyzes the hydroamination of olefins with ammonia to produce a range of amine derivatives. A mechanistic feature for the observed catalytic reaction was discussed with respect to the probed aminoalkyl derivative of palladium(II).

4. Experimental

4.1. General methods and materials

All preparations of air sensitive compounds were performed on a standard Schlenk line or in an inert atmosphere glovebox under argon. THF and diethyl ether were freshly distilled from sodium/benzophenone ketyl under nitrogen and then stored over molecular sieves. Benzene, *n*-hexane, and *n*-pentane were distilled from sodium/



Scheme 7. Plausible reaction pathways for the observed hydroamination of olefins with ammonia in the presence of $Pd(2,6-(Cy_2PCH_2)_2C_6H_3)(OTf)$, involving an aminoalkyl Pd(II) species (pathway A) or a Pd(IV) hydride (pathway B).

benzophenone ketyl in the presence of tetraglyme. CH_2Cl_2 was dried by refluxing over $LiAlH_4$ or CaH_2 under N_2. $PdCl_2$ was supplied by the Pressure Chemical Company and used as received. 1,5-Cyclooctadiene, dppe, AgOTf, NH_4OTf, α,α′-dibromo-*m*-xylene, dimethyl acetylenedicarboxylate (dmad), diethyl acetylenedicarboxylate (dead), phenylacetylene, acrylonitrile, dimethyl maleate, diethyl maleate, *cis*-stilbene, and NMR solvents ($CDCl_3$, C_6D_6) were purchased from Aldrich Chemical Company and used as supplied. Dicyclohexylphosphine was obtained from Strem Chemicals Inc. All other reagents were acquired from various commercial companies. $Pd(dppe)Cl_2$ was prepared by the displacement of cyclooctadiene from $Pd(cod)Cl_2$ with dppe. Complexes of *trans*-$Pd(PEt_3)_2(Ph)Cl$ [28], $Pd(2,6-(Cy_2PCH_2)_2C_6H_3)(OTf)$ [29], *trans*-$[Pd(PEt_3)_2(Ph)(NH_3)]OTf$, $[Pd(dppe)(NH_3)_2](OTf)_2$, and $[Pd(2,6-(Cy_2PCH_2)_2C_6H_3)(NH_3)]OTf$ were prepared using the procedures reported elsewhere [30].

4.2. Physical measurements

The IR spectra were recorded on a Bruker (Tensor 37) FT-IR spectrometer, as a pressed KBr pellets. The ^1H, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were measured on a Varian Gemini-2000 spectrometer (^1H (199.975 MHz), $^{13}C\{^1H\}$ (50.288 MHz), $^{19}F\{^1H\}$ (188.140 MHz), $^{31}P\{^1H\}$ (80.950 MHz)), using the deuterium signal of the solvent as the internal lock frequency. The chemical shifts for ^1H and $^{13}C\{^1H\}$ NMR are reported in parts per million (δ) relative to TMS (Me_4Si). For $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy, the chemical shifts were measured in parts per million relative to external perfluoromethylbenzene ($\delta = -63.73$) and 85% H_3PO_4 in a sealed capillary, respectively. GC–MS was performed using an HP 6890 gas chromatograph equipped with an HP 5973 MSD and an HP-Ultra 1 column (Crosslinked Methyl Silicone Gum, 50 m × 0.2 mm, 0.33 μm film thickness). The injection temperature was 250 °C, and the column temperature ramped from 40 to 250 °C at 10°/min. The conductivity measurements were taken using a TOA conductivity meter (CM-40S). Nitromethane was used as the solvent in a cell containing platinized electrodes (cell constant = 1.014 cm^{-1}). Elemental analyses were performed at the Korea Basic Science Institute in Seoul, Korea.

4.3. Synthesis

4.3.1. anti-$[Pd(PEt_3)(Ph)(\mu-NH_2)]_2$ (**1**)

In a glovebox under an argon atmosphere, a mixture of *trans*-$[Pd(PEt_3)_2(Ph)(NH_3)]OTf$ (500 mg, 0.85 mmol) and $NaNH_2$ (150 mg, 3.8 mmol) was stirred in THF (20 mL) for 6 h at ambient temperature. The color of the reaction suspension was changed slowly from light gray to deep gray during the course of the reaction. The resulting suspension was filtered under vacuum to give a pale yellow solution. The removal of all volatiles from the filtrate under high vacuum resulted in yellow residues, which were extracted with *n*-pentane (4 × 10 mL) to give a pale yellow solution. The volume of solution was reduced to ca. 10 mL to slowly give colorless precipitates, which were filtered, washed with cold *n*-pentane, and dried in vacuo. Yield 176 mg (65%). IR (KBr): ν(NH) = 3238, 3367 cm^{-1} (w, br). ^{1}H NMR (C_6D_6): δ −1.35 (br, 4H, NH_2), δ 0.93 (m, 18H, CH_3), δ 1.09 (m, 12H, CH_2), δ 7.08 (t, 2H, *p*-C*H* (Ph), ^3J(HH) = 7.3 Hz), δ 7.26 (t, 4H, *m*-C*H* (Ph), ^3J(HH) = 7.3 Hz), δ 7.78 (d, 4H, *o*-C*H* (Ph), ^3J(HH) = 7.3 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 8.22 (s, CH_3), δ 15.61 (d, CH_2, ^1J(CP) = 26.7 Hz), δ 122.3, 127.1, 137.6. ^{31}P{^{1}H} NMR (C_6D_6): δ 20.2 (s). Anal. Calcd for $C_{24}H_{44}N_2P_2Pd_2$: C, 45.4; H, 6.98; N, 4.41. Found: C, 45.1; H, 6.84; N, 4.20.

*4.3.2. [Pd(dppe)(μ-NH$_2$)]$_2$(OTf)$_2$ (**2**)*

$NaNH_2$ (170 mg, 4.36 mmol) was added to a stirred solution of [Pd(dppe)(NH_3)$_2$](OTf)$_2$ (1.20 g, 1.43 mmol) in THF at −78 °C (dry ice/acetone). The reaction mixture was stirred for 2 h. The solvent was evaporated to dryness under high vacuum at ca. −20 °C (caution should be taken at this step that the solution temperature should be controlled so as not to exceed more than −20 °C while the solvent was removed, otherwise the color of the solution changed rapidly from colorless to deep-purple, resulting in decomposed species; see Section 2). The residue was extracted with CH_2Cl_2 (3 × 5 mL) giving a pale yellow solution. The solution volume was reduced to ca. 3 mL. The addition of diethyl ether (10 mL) to the concentrated solution gave colorless crystals, which were washed with diethyl ether and dried in vacuo. Yield: 642 mg (67%). IR (KBr): ν(NH) = 3250, 3360 cm^{-1} (w, br), $\nu(SO_3)$ = 1154, 1266 (s, br). ^{1}H NMR ($CDCl_3$): δ −0.19 (br, 4H, NH_2), δ 2.52 (m, 8H, CH_2), δ 7.4–7.7 (m, 40H, Ph). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 53.2 (s) ^{19}F{^{1}H} NMR ($CDCl_3$): δ −78.9 (s). Anal. Calcd for $C_{54}H_{52}F_6N_2O_6P_4Pd_2S_2$: C, 48.41; H, 3.91; N, 2.09; S, 4.79. Found: C, 48.10; H, 4.11; N, 1.77; S, 4.73. $\Lambda_M = 184\ \Omega^{-1}\ cm^2\ mol^{-1}$ (CH_3NO_2, [Pd] = 0.50×10^{-3} M).

*4.3.3. Pd(2,6-(Cy$_2$PCH$_2$)$_2$C$_6$H$_3$)(NH$_2$) (**3**)*

Under similar reaction conditions as for complex **1**, a mixture of [Pd(2,6-(Cy_2PCH_2)$_2$$C_6H_3$)($NH_3$)]OTf (500 mg, 0.65 mmol) and $NaNH_2$ (100 mg, 2.6 mmol) was stirred in THF (30 mL). The color of the reaction mixture was changed slowly from light gray to pale yellow during the course of the reaction. After 4 h, the resulting mixture was filtered under vacuum to give a yellow solution. The removal of all volatiles from the filtrate under high vacuum resulted in orange residues, which were extracted with *n*-hexane (4 × 5 mL) to give a pale yellow solution. The removal of solvent from the extracted solution under high vacuum gave a spectroscopically pure compound of Pd(2,6-(Cy_2PCH_2)$_2$$C_6H_3$)($NH_2$). Yield 270 mg (68%). Spectral data for Pd(2,6-(Cy_2PCH_2)$_2$$C_6H_3$)($NH_2$) (**4**): ^{1}H NMR ($C_6D_6$): δ −0.20 (br, 2H, NH_2), δ 1.0–2.4 (m, 44H, Cy), δ 3.10 (vt, 4H, CH_2, $|^2J(PH) + {}^4J(PH)|$ = 8.4 Hz), δ 7.08 (m, 3H, C*H*(aryl)). ^{31}P{^{1}H} NMR (C_6D_6): δ 50.7 (s).

*4.4. Stoichiometric reactions of **3** with various electrophiles*

The NMR sample preparation for the stoichiometric reactions of complex **3** with various electrophiles was performed in a glovebox under an argon atmosphere. An NMR sample was prepared by the addition of reactant into a d_6-benzene solution of **3** using a 5 mm screw-capped NMR tube (Wilmad, 528-TR) or a 5 mm vacuum NMR tube (Wilmad, 507-LPV). The reaction products were analyzed by NMR (^{1}H, ^{13}C, ^{19}F, and ^{31}P) spectroscopy and GC–MS.

*4.4.1. Reaction of **3** with H$_2$O to yield Pd(2,6-(Cy$_2$PCH$_2$)$_2$C$_6$H$_3$)(OH) (**4**)*

A d_6-benzene (0.3 mL) solution of **3** (ca. 10 mg) in a 5 mm screw-capped NMR tube prepared in a glovebox was removed and stored at ambient temperature. The reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy, showing that complex **3** reacts slowly (over a period of days) with trace amounts of H_2O in solution to give Pd(2,6-(Cy_2PCH_2)$_2$$C_6H_3$)(OH) (**4**). The hydroxo complex Pd(2,6-(Cy_2PCH_2)$_2$$C_6H_3$)(OH) can be prepared independently by a reaction of Pd(2,6-(Cy_2PCH_2)$_2$$C_6H_3$)(OTf) with KOH in THF. The prepared hydroxo complex was characterized by ^{1}H and ^{31}P NMR spectroscopy. For the microanalytical data, the hydrogen content was in good agreement with the calculated values but the carbon value was deviated slightly from an acceptable range because of its instability in air. The data is included as a reference. Treatment of the d_6-benzene solution of **3** with an excess of water resulted in two species, exhibiting the ^{31}P NMR resonances at δ 52.7 (minor) and 54.7 (predominant). The former can be attributed to a cationic ammine species [Pd(2,6-(Cy_2PCH_2)$_2$$C_6H_3$)($NH_3$)]$^+$ by the observation of identical ^{31}P{^{1}H} NMR to that of [Pd(2,6-(Cy_2PCH_2)$_2$$C_6H_3$)($NH_3$)](OTf) at δ 52.7 in d_6-benzene. The latter was attributed to cationic aqua complex [Pd(2,6-(Cy_2PCH_2)$_2$$C_6H_3$)($OH_2$)]$^+$, as evidenced by the identical ^{31}P{^{1}H} NMR at δ 54.7 to a complex prepared from Pd(2,6-(Cy_2PCH_2)$_2$$C_6H_3$)($BF_4$) and H_2O in d_6-benzene. For Pd(2,6-(Cy_2PCH_2)$_2$$C_6H_3$)(OH), ^{1}H NMR ($C_6D_6$): −1.22 (t, 1H, O*H*, ^3J(PH) = 3.3 Hz), 0.8–2.5 (m, 44H, Cy), 3.00 (vt, 4H, CH_2, $|^2J(PH) + {}^4J(PH)|$ = 8.2 Hz), 7.1 (m, 3H, C*H*(aryl)). ^{31}P{^{1}H} NMR (C_6D_6): δ 48.7 (s). Anal. Calcd for $C_{32}H_{52}O_1P_2Pd$: C, 61.9; H, 8.44. Found: C, 59.3; H, 8.64. For [Pd(2,6-(Cy_2PCH_2)$_2$$C_6H_3$)($NH_3$)](OTf): ^{31}P{^{1}H} NMR: 52.7 (s, C_6D_6), 52.4 (s, $CDCl_3$).

*4.4.2. Reaction of **3** with [Ph$_2$I](SO$_3$CF$_3$) or [Ph$_2$I]Cl*

A slight excess amount of [Ph_2I]OTf or [Ph_2I]Cl was added to a d_6-benzene (0.3 mL) solution of **3** (15 mg, 0.024 mmol) in a 5 mm screw-capped NMR tube. The reaction of **3** with [Ph_2I]OTf produced a cationic aniline complex [Pd(2,6-(Cy_2PCH_2)$_2$$C_6H_3$)($NH_2Ph$)]OTf, which was confirmed by its independent preparation from the reaction of Pd(2,6-(Cy_2PCH_2)$_2$$C_6H_3$)OTf and NH_2Ph, showing an identical ^{31}P NMR peak at δ 52.1 in d_6-benzene. On the other hand, attempts at isolating the cationic aniline species were unsuccessful because of dissociation of the coordinated aniline converting to Pd(2,6-(Cy_2PCH_2)$_2$$C_6H_3$)(OTf), which displays a single ^{31}P{^{1}H} NMR at δ 54.5 in d_6-benzene. The reaction of **3** with [Ph_2I]Cl produced Pd(2,6-($Cy_2PCH_2)_2C_6H_3$)Cl ($^{31}P\{^1H\}$ NMR (C_6D_6): δ 52.3) along with the liberated NH_2Ph (GC–MS: m/z = 93, 66, 39).

4.4.3. Reaction of **3** with phenylacetylene to yield Pd(2,6-($Cy_2PCH_2)_2C_6H_3$)(C≡CPh) (**5**)

A slight excess of phenylacetylene (HC≡CPh) was added to a d_6-benzene (0.3 mL) solution of **3** (15 mg, 0.024 mmol) in a 5 mm screw-capped NMR tube. The reaction proceeded readily, in 30 min, to yield the palladium(II) acetylenide Pd(2,6-($Cy_2PCH_2)_2C_6H_3$)(C≡CPh) (**5**), quantitatively. The acetylenido complex is extremely soluble in conventional organic solvents including *n*-pentane. Therefore, the removal of all volatiles from the reaction mixture resulted in a pale yellow solid, which was characterized by IR and NMR (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$) spectroscopy. A preparative scale experiment for this reaction was conducted in a glovebox as follows: an excess amount of phenylacetylene (0.02 g, 0.38 mmol) was added to a benzene solution of **3** (150 mg, 0.24 mmol). The reaction mixture was stirred for 1 h. All volatiles were removed under high vacuum to give yellowish residues. The residues were dissolved in *n*-pentane. The *n*-pentane solution was filtered through a Celite column to give a pale yellow solution. The resulting solution was dried completely under high vacuum to remove all volatiles, yielding an analytically pure compound of Pd(2,6-($Cy_2PCH_2)_2C_6H_3$)(C≡CPh). Spectral data for Pd(2,6-($Cy_2PCH_2)_2C_6H_3$)(C≡CPh) (**5**): IR (KBr): ν(C≡C) = 2096 cm^{-1} ^1H NMR (C_6D_6): δ 1.0–2.4 (m, 44H, Cy), δ 3.20 (vt, 4H, CH_2, $|^2J(PH) + {}^4J(PH)|$ = 8.1 Hz), δ 7.00 (t, 1H, *p*-H(Ph), $^3J(HH)$ = 7.4 Hz), δ 7.2 (m, 3H, C*H* (aryl)), δ 7.21 (m, 2H, *m*-H(Ph)), δ 7.74 (d, 2H, *o*-H(Ph), $^3J(HH)$ = 7.0 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 113.1 (t, Pd–*C*≡CPh, $^2J(CP)$ = 12 Hz), δ 118.3 (Pd–C≡*C*Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 56.4 (s). Anal. Calcd for $C_{40}H_{56}P_2Pd$: C, 68.1; H, 8.00. Found: C, 68.5; H, 7.89.

4.4.4. Reaction of **3** with dialkyl acetylenedicarboxylate (RC≡CR; R = CO_2Me, CO_2Et) to yield (Z)-Pd(2,6-($Cy_2PCH_2)_2C_6H_3$)(CR=CR(NH_2)) (R = CO_2Me (**6a**), CO_2Et (**6b**))

To a d_6-benzene (0.3 mL) solution of **3** (15 mg, 0.024 mmol) in a 5 mm screw-capped NMR tube was added a slight excess of dialkyl acetylenedicarboxylate (RC≡CR; R = CO_2Me, CO_2Et: 0.032 mmol; 0.1 mL of a diluted d_6-benzene solution, which was prepared by the addition of dmad (46 mg) or dead (54 mg) into 1.0 mL of d_6-benzene). The insertion product Pd(2,6-($Cy_2PCH_2)_2C_6H_3$)(CR=CR(NH_2)) was formed quantitatively from the reaction, which was monitored by NMR spectroscopy. The product was barely isolated from the solution because of its high solubility in most organic solvents. Therefore, the removal of all volatiles from the solution under high vacuum resulted in yellow solids, which afforded satisfactory FABMS data. For Pd(2,6-($Cy_2PCH_2)_2C_6H_3$)((MeO_2C)C=C(CO_2Me)(NH_2)) (**6a**): ^1H NMR (C_6D_6): δ 1.0–2.4 (m, 44H, Cy), δ 3.49 (s, 3H, CH_3), δ 3.73 (s, 3H, CH_3), δ 3.10 (dt, H_a, CH_2, $^2J(H_aH_b)$ = 17.6 Hz, $|^2J(PH) + {}^4J(PH)|$ = 7.9 Hz), δ 3.31 (dt, H_b, CH_2, $^2J(H_aH_b)$ = 17.6 Hz, $|^2J(PH) + {}^4J(PH)|$ = 7.9 Hz), δ 3.89 (br, 2H, NH_2), δ 7.21 (m, 3H, C*H* (aryl)). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 50.53, 51.45 (s, CO_2CH_3), δ 162.08, 176.40 (*C*O_2CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 51.7 (s). FABMS (observed m/z 761.22): calcd for $C_{38}H_{59}NO_4P_2Pd$, 761.30. For Pd(2,6-($Cy_2PCH_2)_2C_6H_3$)((EtO_2C)C=C(CO_2Et)(NH_2)) (**6b**): ^1H NMR (C_6D_6): δ 1.0–2.4 (m, 44H, Cy), δ 1.08 (t, 3H, CH_3, $^3J(HH)$ = 7.1 Hz), δ 1.34 (t, 3H, CH_3, $^3J(HH)$ = 7.1 Hz), δ 4.12 (q, 2H, CH_2, $^3J(HH)$ = 7.1 Hz), δ 4.31 (q, 2H, CH_2, $^3J(HH)$ = 7.1 Hz), δ 3.10 (dt, H_a, CH_2, $^2J(H_aH_b)$ = 17.6 Hz, $|^2J(PH) + {}^4J(PH)|$ = 8.3 Hz), δ 3.30 (dt, H_b, CH_2, $^2J(H_aH_b)$ = 17.6 Hz, $|^2J(PH) + {}^4J(PH)|$ = 8.3 Hz), δ 3.94 (br, 2H, NH_2), δ 7.21 (m, 3H, C*H*(aryl)). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 14.47, 15.15 ($CO_2CH_2CH_3$), δ 58.98, 60.30 ($CO_2CH_2CH_3$), δ 162.08, 176.09 (*C*$O_2CH_2CH_3$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 51.9 (s). FABMS (observed m/z 789.25): calcd for $C_{40}H_{63}NO_4P_2Pd$, 789.33.

4.4.5. Reaction of (Z)-Pd(2,6-($Cy_2PCH_2)_2C_6H_3$)(CR=CR(NH_2)) (R = CO_2Me (**6a**), CO_2Et (**6b**)) with HOC_6H_4-p-NO_2 to yield cis-CHR=CR(NH_2) (R = CO_2Me, CO_2Et) and Pd(2,6-($Cy_2PCH_2)_2C_6H_3$)(OC_6H_4-p-NO_2) (**7**)

HOC_6H_4-*p*-NO_2 (5 mg) was added to a d_6-benzene (0.3 mL) solution of **6a** or **6b** (ca. 15 mg) in a 5 mm screw-capped NMR tube. The reaction proceeded quantitatively to produce *cis*-CHR=CR(NH_2) (R = CO_2Me, CO_2Et) and Pd(2,6-($Cy_2PCH_2)_2C_6H_3$)(OC_6H_4-*p*-NO_2) (**7**). All products were analyzed by ^1H and ^{31}P NMR spectroscopy, and GC–MS. The *p*-nitrophenoxide complex Pd(2,6-($Cy_2PCH_2)_2C_6H_3$)(OC_6H_4-*p*-NO_2) (**7**) was prepared independently from an equimolar reaction of Pd(2,6-($Cy_2PCH_2)_2C_6H_3$)(OTf) and $NaOC_6H_4$-*p*-NO_2 in THF. For *cis*-((MeO_2C)CH=C(CO_2Me)(NH_2)): ^1H NMR (C_6D_6): δ 3.15 (s, 3H, CH_3), δ 3.44 (s, 3H, CH_3), δ 5.77 (s, 1H, C*H*). GC–MS: m/z = 159, 128, 100, 68, 59. For *cis*-((EtO_2C)CH=C(CO_2Et)(NH_2)): ^1H NMR (C_6D_6): δ 0.78 (t, 3H, CH_3, $^3J(HH)$ = 7.13 Hz), δ 1.02 (t, 3H, CH_3, $^3J(HH)$ = 7.13 Hz), δ 3.79 (q, 2H, CH_2, $^3J(HH)$ = 7.13 Hz), δ 4.07 (q, 2H, CH_2, $^3J(HH)$ = 7.13 Hz), δ 5.84 (s, 1H, C*H*). GC–MS: m/z = 187, 142, 114, 86, 68. For Pd(2,6-($Cy_2PCH_2)_2C_6H_3$)(OC_6H_4-*p*-NO_2) (**7**): IR (KBr): ν(NO) = 1583, 1303 cm^{-1} (sh, s). ^1H NMR (C_6D_6): δ 0.9–2.1 (m, 44H, Cy), δ 2.84 (vt, 4H, CH_2, $|^2J(PH) + {}^4J(PH)|$ = 8.4 Hz), δ 6.88 (d, 2H, $^3J(HH)$ = 9.2 Hz), δ 8.49 (d, 2H, $^3J(HH)$ = 9.2 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 50.7 (s). Anal. Calcd for $C_{38}H_{55}NO_3P_2Pd$: C, 61.5; H, 7.47; N, 1.89. Found: C, 61.1; H, 7.52; N, 1.58.

4.4.6. Reaction of dialkyl acetylenedicarboxylate with ammonia

Anhydrous gaseous ammonia was bubbled into a d_6-benzene (0.3 mL) solution of dialkyl acetylenedicarboxylate (dmad, dead; ca. 20 mg, respectively) for ca. 30 s in a 5 mm screw-capped NMR tube. The reaction produced an isomeric mixture of *cis*- and *trans*-(CHR=CR(NH_2)) in a *trans*/*cis* ratio of ca. 1.3. For *trans*-((MeO_2C)CH=C(CO_2Me)(NH_2)): ^1H NMR (C_6D_6): δ 3.42 (s, 3H, CH_3), δ 3.59 (s, 3H, CH_3), δ 4.80 (s, 1H, C*H*). For *trans*-((EtO_2C)CH=C(CO_2Et)(NH_2)): ^1H NMR (C_6D_6): δ 0.75 (t, 3H, CH_3, $^3J(HH)$ = 7.13 Hz), δ 1.01 (t, 3H, CH_3, $^3J(HH)$ = 7.13 Hz), δ 3.37 (q, 2H, CH_2), δ 4.08 (q, 2H, CH_2), δ 4.90 (s, 1H, C*H*). For *cis*-((MeO_2C)CH=C(CO_2Me)(NH_2)) and *cis*-((EtO_2C)CH=C(CO_2Et)(NH_2)) refer to the preceding experiment.

4.4.7. Reaction of **3** with dialkyl maleate (cis-(CO_2R)CH=CH(CO_2R)) (R = CH_3, CH_2CH_3)

An excess of dialkyl maleate (*cis*-(CO_2R)CH=CH(CO_2R), R = CH_3, CH_2CH_3) was added to a d_6-benzene (0.3 mL) solution of **3** (15 mg, 0.024 mmol) in a 5 mm screw-capped NMR tube. The dialkyl maleate slowly isomerizes to dialkyl fumarate (*trans*-(CO_2R)CH=CH(CO_2R), R = CH_3, CH_2CH_3) in the presence of catalytic amounts of **3** at ambient temperature, as evidenced by ^1H NMR spectroscopy. After 4 h, the observed *trans*/*cis* ratio was 0.8 (for R = Me) and 0.7 (for R = Et), respectively. After 24 h, the *trans*/*cis* ratio was 8.9 (for R = Me). The conversion of dialkyl maleate (*cis*-isomer) into dialkyl fumarate (*trans*-isomer) was complete in 5 days. For dimethyl maleate (*cis*-(CO_2CH_3)CH=CH(CO_2CH_3)): ^1H NMR (C_6D_6): δ 3.35 (s, 6H, CH_3), δ 5.71 (s, 2H, C*H*). For dimethyl fumarate (*trans*-(CO_2CH_3)CH=CH(CO_2CH_3)): ^1H NMR (C_6D_6): δ 3.25 (s, 6H, CH_3), δ 6.87 (s, 2H, C*H*). For diethyl maleate (*cis*-($CO_2CH_2CH_3$)CH=CH($CO_2CH_2CH_3$)): ^1H NMR (C_6D_6): δ 0.96 (t, 6H, CH_3, ^3J(HH) = 9.2 Hz), δ 3.98 (q, 4H, CH_2, ^3J(HH) = 9.2 Hz), δ 5.77 (s, 2H, C*H*). For diethyl fumarate (*trans*-($CO_2CH_2CH_3$)CH=CH($CO_2CH_2CH_3$)): ^1H NMR (C_6D_6): δ 0.89 (t, 6H, CH_3, ^3J(HH) = 7.6 Hz), δ 3.88 (q, 4H, CH_2, ^3J(HH) = 7.6 Hz), δ 6.91 (s, 2H, C*H*).

4.4.8. Reaction of 3 with cis-stilbene

An excess of *cis*-stilbene (*cis*-CHPh=CHPh) was added to a d_6-benzene (0.3 mL) solution of **3** (15 mg, 0.024 mmol) in a 5 mm screw-capped NMR tube. No reaction occurred at ambient temperature for 10 h. At an increased temperature of 50 °C (in a silicone oil bath), however, *cis*-stilbene isomerized catalytically to *trans*-stilbene in the presence of **3**: *trans*/*cis* = 2.0 for 2 h. For *cis*-stilbene (*cis*-CHPh=CHPh), ^1H NMR (C_6D_6): δ 6.49 (s, (2H, C*H*). For *trans*-stilbene (*trans*-CHPh=CHPh), ^1H NMR (C_6D_6): δ 7.02 (s, 2H, C*H*).

4.4.9. Reaction of 3 with acrylonitrile

A slight excess of acrylonitrile (ca. 1.5 μL) was added to a d_6-benzene (0.3 mL) solution of **3** (15 mg, 0.024 mmol) in a 5 mm screw-capped NMR tube via a microsyringe. The reaction proceeded readily to generate a metastable addition product Pd(2,6-($Cy_2PCH_2)_2C_6H_3$)(CH(CN)CH_2NH_2). Attempts at isolating the addition product from the solution were unsuccessful because of decomposition to a couple of unidentified species. On the other hand, in the reaction of **3** with a large excess of acrylonitrile, the addition product gradually disappeared to give a couple of new complexes, as evidenced by ^{31}P NMR spectroscopy, along with the generation of insoluble polymeric species of acrylonitrile in solution. After filtration of the precipitates, the ^{31}P NMR spectrum of the solution exhibited a couple of new resonances, one at δ 59.2 corresponding to a cationic acrylonitrile complex [Pd(2,6-($Cy_2PCH_2)_2C_6H_3$)(CH_2=CHCN)]$^+$, which can be verified by the reaction of Pd(2,6-($Cy_2PCH_2)_2C_6H_3$)(OTf) with CH_2=CHCN (excess) in d_6-benzene. Spectral data for Pd(2,6-($Cy_2PCH_2)_2C_6H_3$)(CH(CN)CH_2NH_2): ^1H NMR (C_6D_6): δ 1.0–2.4 (m, 44H, Cy), ca. δ 2.2 (m, C*H*), ca. δ 3.1 (m, CH_a), ca. δ 3.5 (m, CH_b), δ 3.16 (vt, 4H, CH_2, $|^2J(PH) + ^4J(PH)| = 8.1$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 49.0 (s). For polymeric species: IR (KBr): ν(CN) = 2245, 2204 cm^{-1}, ν(NH_2) = 3300, 3360 cm^{-1}. For [Pd(2,6-($Cy_2PCH_2)_2C_6H_3$)(CH_2=CHCN)](OTf), $^{31}P\{^1H\}$ NMR: δ 59.2 (C_6D_6), δ 59.4 ($CDCl_3$).

4.5. A typical procedure for catalytic hydroamination of olefins with ammonia

The catalytic hydroamination of olefins with ammonia in the presence of Pd(2,6-($Cy_2PCH_2)_2C_6H_3$)(OTf) was performed in two ways. Method A using a 5 mm vacuum NMR tube (Wilmad, 507-LPV): anhydrous ammonia was introduced into a d_6-benzene (0.5 mL) solution of Pd(2,6-($Cy_2PCH_2)_2C_6H_3$)(OTf) (3 mg, 3.98×10^{-3} mmol) and CH_2=CHCN (0.026 mL, 3.98×10^{-1} mmol) in a 5 mm vacuum NMR tube, which was precooled and evacuated via several freeze and thaw cycles. The molar ratio of CH_2=CHCN/NH_3 was calculated by integrating the corresponding resonance peaks in the ^1H NMR spectrum of the prepared sample. The NMR sample was kept in silicone oil for 12 h at 60 °C. After cooling the sample, the reaction products were analyzed by ^1H NMR spectroscopy and GC–MS. For GC–MS analysis, the reaction mixture was transferred to a short glass-column (0.7 × 15 cm) packed with alumina (ca. 1 cm). Eluting the mixture with diethyl ether resulted in a clear pale yellow solution, which was analyzed by GC–MS. Method B using a high pressure reactor (Carl Roth, Model 1, 100 mL): a mixture of Pd(2,6-($Cy_2PCH_2)_2C_6H_3$)(OTf) (3 mg, 3.98×10^{-3} mmol) and CH_2=CHCN (0.026 mL, 3.98×10^{-1} mmol) in d_6-benzene (0.5 mL) was loaded in a glass linear equipped with a high pressure reactor. The reactor was then cooled at −15 °C (ice/NaCl) and evacuated. Anhydrous ammonia gas was introduced into the reactor for 5 min at 0 °C to reach a pressure of 8 atm. When reactor temperature was increased to 60 °C, the pressure increased to 25 atm. The reaction mixture was stirred for 12 h at 60 °C. After cooling the reactor in an ice bath, gaseous ammonia was removed from the reactor in a well ventilating hood. The reaction products were analyzed by ^1H NMR spectroscopy and GC–MS in a similar manner. Spectral data for CH_2(CN)CH_2NH_2, ^1H NMR (C_6D_6): δ 1.45 (t, 2H, CH_2CN, ^3J(HH) = 6.4 Hz), δ 2.13 (t, 2H, CH_2N, ^3J(HH) = 6.4 Hz). GC–MS: m/z = 69, 42, 30, 28. For (CH_2(CN)$CH_2)_2$NH, ^1H NMR (C_6D_6): δ 1.50 (t, 4H, CH_2CN, ^3J(HH) = 6.4 Hz), δ 1.97 (t, 4H, CH_2N, ^3J(HH) = 6.4 Hz). GC–MS: m/z = 123, 83, 54, 42, 30, 28. For (CH_2(CN)$CH_2)_3$N, ^1H NMR (C_6D_6): δ 1.59 (t, 6H, CH_2CN, ^3J(HH) = 6.8 Hz), δ 1.94 (t, 6H, CH_2N, ^3J(HH) = 6.8 Hz). GC–MS: m/z = 176, 136, 109, 83, 54, 42, 30. For (CH_2(CN)CH(CH_3))NH_2, GC–MS: m/z = 83, 69, 44, 42, 40, 28, 18, 15. For (CH_2(CO_2CH_3)$CH_2)_2$NH, GC–MS: m/z = 187, 174, 157, 130, 102, 56. For (CH_2(CO_2CH_3)$CH_2)_3$N, GC–MS: m/z = 275, 216, 157, 101, 56.

4.6. X-ray structure determination

All X-ray data collections were performed using Mo Kα radiation (λ = 0.71069 Å) on an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal, incident beam monochromator. All calculations were carried out using the SHELX-97 programs [31]. All structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were generated in ideal positions and refined in a riding model.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.crci.2015.12.008.

References

[1] (a) M.D. Fryzuk, C.D. Montgomery, Coord. Chem. Rev. 95 (1989) 1;
(b) H.E. Brynza, W. Tam, Chem. Rev. 88 (1988) 1163;
(c) J.R. Fulton, A.W. Holland, D.J. Fox, R.G. Bergman, Acc. Chem. Res. 35 (2002) 44;
(d) J.F. Hartwig, Nature 455 (2008) 314;
(e) J.P. Wolfe, S. Wagaw, J.F. Marcoux, S.L. Buchwald, Acc. Chem. Res. 31 (1998) 805.

[2] (a) A.L. Casalnuovo, J.C. Calabrese, D. Milstein, J. Am. Chem. Soc. 110 (1988) 6738;
(b) R.L. Cowan, W.C. Trogler, J. Am. Chem. Soc. 111 (1989) 4750;
(c) J.F. Hartwig, R.G. Bergman, R.A. Andersen, J. Am. Chem. Soc. 113 (1991) 6499;
(d) G.C. Martin, G.J. Palenik, J.M. Boncella, Inorg. Chem. 29 (1990) 2027;
(e) A.L. Seligson, R.L. Cowan, W.C. Trogler, Inorg. Chem. 30 (1991) 3371;
(f) Y.-W. Ge, F. Peng, P.R. Sharp, J. Am. Chem. Soc. 112 (1990) 2632;
(g) C. Ye, P.R. Sharp, Inorg. Chem. 34 (1995) 55;
(h) M.J. Fernandez, J. Modrego, F.J. Lahoz, J.A. López, L.A. Oro, J. Chem. Soc., Dalton Trans. (1990) 2587;
(i) M.K. Kolel-Veetil, A.L. Rheingold, K.J. Ahmed, Organometallics 12 (1993) 3439;
(j) J.-J. Brunet, G. Commenges, D. Neibecker, K. Philippot, L. Rosenberg, Inorg. Chem. 33 (1994) 6373;
(k) Y.-J. Kim, J.-C. Choi, K. Osakada, J. Organomet. Chem. 491 (1995) 97;
(l) J. Ruiz, M.T. Martinez, C. Vicente, G. Garcia, G. Lopez, P.A. Chaloner, P.B. Hitchcock, Organometallics 12 (1993) 4321;
(m) J.F. Hartwig, J. Am. Chem. Soc. 118 (1996) 7010;
(n) M.S. Driver, J.F. Hartwig, J. Am. Chem. Soc. 118 (1996) 4206;
(o) D.D. VanderLende, K.A. Abboud, J.M. Boncella, Inorg. Chem. 34 (1995) 5319;
(p) P.L. Holland, R.A. Andersen, R.G. Bergman, J. Am. Chem. Soc. 118 (1996) 1092;
(q) J.V. Cuevas, G. Garcia-Herbosa, A. Munoz, S. Garcia-Granda, D. Miguel, Organometallics 16 (1997) 2220;
(r) H. Matsuzaka, K. Ariga, H. Kase, T. Kamura, M. Kondo, S. Kitagawa, M. Yamasaki, Organometallics 16 (1997) 4514;
(s) J.J. Li, W. Li, A.J. James, T. Holbert, T.P. Sharp, P.R. Sharp, Inorg. Chem. 38 (1999) 1563;
(t) U. Anandhi, T. Holbert, D. Lueng, P.R. Sharp, Inorg. Chem. 42 (2003) 1282;
(u) A. Singh, U. Anandhi, M.A. Cinellu, P.R. Sharp, Dalton Trans. (2008) 2314;
(v) J.F. Hartwig, Inorg. Chem. 46 (2007) 1936;
(w) C. Munro-Leighton, Y. Feng, J. Zhang, N.M. Alsop, T.B. Gunnoe, P.D. Boyle, J.L. Petersen, Inorg. Chem. 47 (2008) 6124;
(x) J.R. Webb, C. Munro-Leighton, A.W. Pierpont, J.T. Gurkin, T.B. Gunnoe, T.R. Cundari, M. Sabat, J.L. Petersen, P.D. Boyle, Inorg. Chem. 50 (2011) 4195.

[3] (a) I. Mena, E.A. Jaseer, M.A. Casado, P. Garcia-Orduna, F.J. Lahoz, L.A. Oro, Chem. Eur. J. 19 (2013) 5665;
(b) A.L. Casalnuovo, J.C. Calabrese, D. Milstein, Inorg. Chem. 26 (1987) 973;
(c) F.P. Rotzwinger, W. Marty, Inorg. Chem. 22 (1983) 3593;
(d) M. Kretschmer, L.Z. Heck, Anorg. Allg. Chem. 490 (1982) 215;
(e) N.J. Curtis, K.S. Hagen, A.M. Sargeson, Inorg. Chem. 23 (1984) 1571;
(f) L. Heck, M. Ardon, A. Bino, J. Zaap, J. Am. Chem. Soc. 110 (1988) 2691;
(g) M.G. Scheibel, J. Abbenseth, M. Kinauer, F.W. Heinemann, C. Würtele, B. de Bruin, S. Schneider, Inorg. Chem. 54 (2015) 9290.

[4] (a) G.C. Dobinson, R. Mason, G.B. Robertson, R.U.F. Conti, D. Morelli, S. Cenini, F. Bonati, J. Chem. Soc., Chem. Comm. (1967) 739;
(b) N.W. Alcock, P. Bergamini, T.J. Kemp, P.G. Pringle, S. Sostero, O. Traverso, Inorg. Chem. 30 (1991) 1594;
(c) C.A. O'Mahoney, I.P. Parkin, D.J. Williams, J.D. Woollins, Polyhedron 8 (1989) 1979.

[5] (a) S. Park, A.L. Rheingold, D.M. Roundhill, Organometallics 10 (1991) 615;
(b) F.L. Joslin, M.P. Johnson, J.T. Mague, D.M. Roundhill, Organometallics 10 (1991) 2781;
(c) R. Koelliker, D. Milstein, J. Am. Chem. Soc. 113 (1991) 8524;
(d) J.R. Fulton, S. Sklenak, M.W. Bouwkamp, R.G. Bergman, J. Am. Chem. Soc. 124 (2002) 4722;
(e) D.J. Fox, R.G. Bergman, J. Am. Chem. Soc. 125 (2003) 8984;
(f) D. Rais, R.G. Bergman, Chem.—Eur. J. 10 (2004) 3970;
(g) D.J. Fox, R.G. Bergman, Organometallics 23 (2004) 1656;
(h) D. Conner, K.N. Jayaprakash, T.R. Cundari, T.B. Gunnoe, Organometallics 23 (2004) 2724;
(i) J. Zhao, A.S. Goldman, J.F. Hartwig, Science 307 (2005) 1080;
(j) T. Braun, Angew. Chem. Int. Ed. 44 (2005) 5012;
(k) D.V. Gutsulyak, W.E. Piers, J. Borau-Garcia, M. Parvez, J. Am. Chem. Soc. 135 (2013) 11776;
(l) Y.-H. Chang, Y. Nakajima, H. Tanaka, K. Yoshizawa, F. Ozawa, J. Am. Chem. Soc. 135 (2013) 11791.

[6] (a) J.I. van der Vlugt, Chem. Soc. Rev. 39 (2010) 2302;
(b) D.M. Roundhill, Chem. Rev. 92 (1992) 1;
(c) G.D. Vo, J.F. Hartwig, J. Am. Chem. Soc. 131 (2009) 11049;
(d) D.S. Surry, S.L. Buchwald, J. Am. Chem. Soc. 129 (2007) 10354;
(e) T. Schulz, C. Torborg, S. Enthaler, B. Schaffner, A. Dumrath, A. Spannenberg, H. Neumann, A. Borner, M. Beller, Chem. Eur. J. 15 (2009) 4528;
(f) R.J. Lundgren, A. Sappong-Kumankumah, M. Stradiotto, Chem. Eur. J. 16 (2010) 1983.

[7] (a) Q. Shen, J.F. Hartwig, J. Am. Chem. Soc. 128 (2006) 10028;
(b) J.L. Klinkenberg, J.F. Hartwig, J. Am. Chem. Soc. 132 (2010) 11830.

[8] (a) S.Y. Ryu, H. Kim, H.S. Kim, S. Park, J. Organomet. Chem. 592 (1999) 194;
(b) J.M. Seul, S. Park, J. Chem. Soc., Dalton Trans. (2002) 1153.

[9] R.S. Paonessa, A.L. Prignano, W.C. Trogler, Organometallics 4 (1985) 647.

[10] J.P. Collman, J.E. Hutchison, M.S. Ennis, M.A. Lopez, R. Guilard, J. Am. Chem. Soc. 114 (1992) 8074.

[11] J.A. Herron, P. Ferrin, M. Mavrikakis, J. Phys. Chem. C 119 (2015) 14692.

[12] K.R. Dixon, A.C. Dixon, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, 9, Pergamon, Oxford, 1995, p. 196.

[13] Precedents of structurally determined bridging arylamido complexes of palladium(II): (a) L.A. Villanueva, K.A. Abboud, J.M. Boncella, Organometallics 13 (1994) 3921;
(b) J. Ruiz, V. Rodriguez, G. Lopez, P.A. Chaloner, P.B. Hitchcock, J. Chem. Soc., Dalton Trans. (1997) 4271;
(c) J. Ruiz, V. Rodriguez, G. Lopez, J. Casabo, E. Molins, C. Miravitlles, Organometallics 18 (1999) 1177.

[14] (a) H.-W. Suh, T.J. Schmeier, N. Hazari, R.A. Kemp, M.K. Takase, Organometallics 31 (2012) 8225;
(b) C.J. Moulton, B.L. Shaw, J. Chem. Soc., Dalton Trans. (1976) 1020.

[15] H.-B. Kraatz, D. Milstein, J. Organomet. Chem. 488 (1995) 223.

[16] J. Campora, P. Palma, D. del Rio, E. Alvarez, Organometallics 23 (2004) 1652.

[17] J. Campora, P. Palma, D. del Rio, M. Mar Conejo, E. Alvarez, Organometallics 23 (2004) 5653.

[18] K. Osakada, R. Sakata, T. Yamamoto, Organometallics 16 (1997) 5354.

[19] H.E. Bryndza, L.K. Fong, R.A. Paciello, W. Tam, J.E. Bercaw, J. Am. Chem. Soc. 109 (1987) 1444.

[20] J. Uddin, C.M. Morales, J.H. Maynard, C.R. Landis, Organometallics 25 (2006) 5566.

[21] (a) L.A. Villanueva, K.A. Abboud, J.M. Boncella, Organometallics 11 (1992) 2963;
(b) P.S. Hanley, D. Marković, J.F. Hartwig, J. Am. Chem. Soc. 132 (2010) 6302;
(c) J.D. Neukom, N.S. Perch, J.P. Wolfe, J. Am. Chem. Soc. 132 (2010) 6276.

[22] H.M. Senn, P.E. Blochl, A. Togni, J. Am. Chem. Soc. 122 (2000) 4098.

[23] S. Stromberg, K. Zetterberg, P.E.M. Siegbahn, J. Chem. Soc., Dalton Trans. (1997) 4147.
[24] A.L. Seligson, W.C. Trogler, Organometallics 12 (1993) 744.
[25] S. Park, Bull. Korean Chem. Soc. 23 (2002) 132.
[26] (a) B. Akermark, J.-E. Backvall, L.S. Hegedus, K. Zetterberg, K. Siirala-Hansen, K. Sjoberg, J. Organomet. Chem. 72 (1974) 127;
(b) C. Hahn, A. Vitagliano, F. Giordano, R. Taube, Organometallics 17 (1998) 2060;
(c) C. Hahn, P. Morvillo, A. Vitagliano, Eur. J. Inorg. Chem. 2 (2001) 419.
[27] P.A. Dub, R. Poli, J. Am. Chem. Soc. 132 (2010) 13799.
[28] R.J. Cross, R. Wardle, J. Chem. Soc. A (1970) 840.
[29] H.J. Lee, S.H. Lee, H.C. Kim, Y.-E. Lee, S. Park, J. Organomet. Chem. 717 (2012) 164.
[30] (a) J.G. Yun, J.M. Seul, K.D. Lee, S. Kim, S. Park, Bull. Korean Chem. Soc. 17 (1996) 311;
(b) J.G. Yun, J.M. Seul, K.D. Lee, S. Kim, S. Park, Bull. Korean Chem. Soc. 17 (1996) 125.
[31] G.M. Sheldrick, SHELX-97, University of Göttingen, Germany, 1993.