Title: An Isolable Mononuclear Palladium(I) Amido Complex

Authors: Jian Liu¹, Melissa M. Bollmeyer², Yujeong Kim^{3,4}, Dengmengfei Xiao⁵, Samantha N. MacMillan², Qi Chen¹, Xuebing Leng¹, Sun Hee Kim^{3,4*}, Lili Zhao^{5*}, Kyle M. Lancaster^{2*}, and Liang Deng^{1*}.

Affiliations:

¹State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China.

²Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY, USA.

³Western Seoul Center, Korea Basic Science Institute (KBSI), Seoul 03759, Republic of Korea.

⁴Department of Chemistry and Nano Science, Ewha Womans University, Seoul 03760, Republic of Korea.

⁵Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 211816, China.

*Correspondence to: shkim7@kbsi.re.kr (S.H.K.), ias_llzhao@njtech.edu.cn (L.Z.), kml236@cornell.edu (K.M.L.), deng@sioc.ac.cn (L.D.).

Abstract:

Mononuclear Pd(I) species are putative intermediates in Pd-catalyzed reactions, but our knowledge about them is limited due to difficulties in accessing them. Herein, we report the isolation of a Pd(I) amido complex, [(BINAP)Pd(NHAr^{Trip})] (BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthalene, Ar^{Trip} = 2,6-bis(2',4',6'-triisopropylphenyl)phenyl), from the reaction of (BINAP)PdCl₂ with LiNHAr^{Trip}. This Pd(I) amido species has been characterized by X-ray crystallography, electron paramagnetic resonance, and multi-edge Pd X-ray absorption spectroscopy. Theoretical study revealed that, while the 3-electron-2-center π -interaction between Pd and N in the Pd(I) complex imposes severe Pauli repulsion in its Pd–N bond, pronounced attractive inter-ligand dispersion force aids its stabilization. In accord with its electronic features, reactions of homolytic Pd–N bond cleavage and deprotonation of primary amines are observed on the Pd(I) amido complex.

One Sentence Summary:

An isolable Pd(I) amido complex was prepared and its electronic structure and reactivity properties characterized.

Main Text:

Palladium is a frequently used metal in the modern molecular chemists' catalyst arsenal, and can be found in a variety of useful organic reactions, such as Wacker oxidations, cross-couplings, C–H bond functionalization and hydrogenation reactions (*1*). Underlying the broad utility of Pd are the multiple oxidation states accessible, which suit them well to the formation and cleavage of covalent bonds. Pd compounds most commonly occur as diamagnetic, closed-shell Pd(0), Pd(II) and Pd(IV) complexes. Paramagnetic, open-shell Pd compounds are far less prevalent, but are now receiving increased attention (*2-5*). Paramagnetic Pd(I) species, for example, are implicated as intermediates in some Pd-catalyzed reactions, but sparse data are

available concerning their electronic structures and reactivity. In Pd-catalyzed C–C bond-forming reactions, Pd(I) halide species $L_nPd^I X$ (L = phosphine; X = Br, I) are proposed to form via single-electron transfer reactions of photo-excited Pd(0) phosphine complexes with organic halides (6–8), as well as in the reactions of Pd(0) phosphine complexes with fluoroalkyl halides (9) (Fig. 1A). In the reactions of Pd(0) species with dioxygen, which is a key step in Pd-catalyzed aerobic oxidation reactions, Pd(I) superoxide species $L_nPd^I(\eta^1-OO^{\bullet})$ are proposed as intermediates en route to Pd(II) peroxides $L_nPd^{II}(\eta^2-O_2)$ (10) (Fig. 1A). The formation of the Pd(I) intermediates has also been envisaged in thermolysis or photolysis of Pd(II) compounds. For example, photolysis-induced decomposition of (PNP)Pd(II) alkyl (PNP = phosphine-amido-phosphine) complexes was proposed to proceed through (PNP)Pd(I) intermediates that dimerized to yield diamagnetic, dinuclear Pd(I) complexes (11) (Fig. 1A).

Fig. 1. Research background on Pd(I) species bearing π -donating ligands. (A) Examples of reactive Pd(I) intermediates containing π -donating ligands. **(B)** Pauli repulsion in metal-ligand π -interaction. **(C)** A cartoon illustrating how London dispersion forces stabilize an M–X bond.

A common feature of the aforementioned reactive Pd(I) intermediates is the presence of π -donors—ligands whose coordinating atoms bear non-bonding lone pairs, *e.g.* halides, superoxide, and amido in the aforementioned cases—within Pd's inner coordination sphere. Such mononuclear Pd(I) species reported to date are exceedingly reactive and have only been observed using spectroscopic methods in γ -ray irradiated Pd(II)Cl₂ and Pd(II)(acac)₂ and thermalized Pd(II)-exchanged zeolites (12–14), where their stability is conferred by immobilization within the lattice framework. Certain Pd(0) and Pd(II) complexes are reported to undergo chemical and electrochemical redox reactions to produce mononuclear paramagnetic Pd(I) complexes (15–19). These include three isolable complexes [(PBU'₃)₂Pd]X (X = PF₆, CB₁₁Cl₁₁H) (18, 19) and [(PBU'₃)₂Pd(NCMe)](CB₁₁Cl₁₁H) (19). These mononuclear Pd(I) complexes, however, are not supported by π -donating ligands. To our knowledge, isolable Pd(I) complexes bearing π -donating ligand have remained elusive. The challenge of accessing mononuclear Pd(I) complexes bearing π -donating ligands likely originates from severe Pauli repulsion: conventional wisdom dictates that π -interactions between the *nd* orbitals of low-valent platinum-group metals (Ru, Rh, Pd, Os, Ir, Pt) and the lone pairs of π -donors (Fig. 1B) should enforce severe Pauli repulsion (20, 21), leading to the destabilization of the metal–ligand

multiple bond. Pauli repulsion has been used to explain the high reactivity of low-valent platinum-group metal amido, alkoxide, imido, oxo, and nitride species (22-24). So far, low-valent platinum-group metal complexes containing π -donor ligands are restricted to the nd^6 - nd^8 metal ions (25-27). Analogous isolable complexes containing a nd^9 -platinum-group metal center are unknown.

Herein we report the first nd^9 platinum-group metal terminal amido complex, namely the Pd(I) complex [(BINAP)Pd(NHAr^{Trip})] (BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthalene, Ar^{Trip} = 2,6-bis(2',4',6'-triisopropylphenyl)phenyl). The Pd(I) amido complex is isolated from the reaction of (BINAP)PdCl₂ with LiNHAr^{Trip} and has been characterized by single-crystal X-ray diffraction, electron paramagnetic resonance spectroscopy, and multi-edge Pd X-ray absorption spectroscopy. Electronic structure calculations indicate that the Pd(I) amido complex is $S = \frac{1}{2}$ with a three-electron two-center π -interaction between the Pd and N atoms, and that the Pd–N bond indeed present severe destabilizing Pauli repulsion. However, dispersion forces (28) (Fig. 1C) between BINAP and the bulky amido ligand aids the stabilization of the complex. Further reactivity studies evaluate the lability of the Pd–N bond. When subjected to thermolysis, photo-irradiation, or coordination of exogenous ligands, the Pd(I) amido complex undergoes homolytic Pd–N bond cleavage to release the aminyl radical [NHAr^{Trip}][•]. In addition, the amido ligand in the Pd(I) complex exhibits high basicity as it can deprotonate primary alkyl and aryl amines. These observations showcase the unique reactivity of low-valent, odd-electron platinum-group-metal amido complexes.

Synthesis and Molecular Structure of [(BINAP)Pd(NHAr^{Trip})]. The Pd(I) amido complex [(BINAP)Pd(NHAr^{Trip})] (**1**) was obtained via the reaction of (BINAP)PdCl₂ with two equivalents of LiNHAr^{Trip}. Mixing the two reagents in toluene at –78 °C produced a blue solution, whose ³¹P NMR spectrum features two signals with an *AB*-splitting pattern, suggesting the formation of a Pd(II) monoamido intermediate, presumably (BINAP)Pd(NHAr^{Trip})Cl (**A**). When warmed to room temperature, the solution turned green. Recrystallization led to the isolation of the Pd(I) amido complex **1** as a green crystalline solid in 51% yield (Fig. 2A). The composition of **1** is supported by elemental analysis (C, H, N), cold electrospray mass spectroscopy (Fig. S6), and its structure has been confirmed by single-crystal X-ray diffraction (Fig. 2B). The infrared spectrum of **1** features an N–H stretch at 3484 cm^{–1}. The deuterated isotopologue [(BINAP)Pd(NDAr^{Trip})] (**1-d**) shows the N–D stretch at 2641 cm^{–1} (Fig. S5). In addition to **1**, three amine byproducts, the amino-imine **2**, the aniline featuring an alkene side arm **3**, and the free aniline **4** (Fig. 2A), are observed. These amines are likely formed from the decomposition reactions of the aminyl radical [NHAr^{Trip}][•]. Consequently, **1** is proposed to form via a homolytic Pd–N bond cleavage reaction of a Pd(II) bisamido intermediate, (BINAP)Pd(NHAr^{Trip})₂, that can be produced by the interaction of **A** with LiNHAr^{Trip} (Fig. 2C).

Fig. 2. Synthetic route to the Pd(I) amido complex and its molecular structure. (A) The reaction giving Pd(I) amido complex [(BINAP)Pd(NHAr^{Tri})] (**1**) and the byproducts **2-4**. **(B)** Molecular structure of **1**, showing one of the two crystallographically independent molecules in the unit cell with 30% displacement ellipsoids and a partial atom numbering scheme. Hydrogen atoms, except the one on N1, are omitted for clarity. Selected distances (Å) and angles (deg): Pd1-N1 2.063(2), Pd1-P1 2.3314(7), Pd1-P2 2.2883(7), N1-C45 1.377(3), P2-Pd1-P1 92.20(2), N1-Pd1-P1 108.06(6), N1-Pd1-P2 154.04(6), C45-N1-Pd1 135.29(18). **(C)** A proposed route for the formation of **1** and the byproducts **2-4**.

Single crystals of **1** were obtained by cooling a diethyl ether solution at $-30\text{ }^{\circ}\text{C}$ for two days. X-ray diffraction revealed that there are two crystallographically independent molecules in the unit cell, with similar structure metrics. As the representative, Fig. 1B depicts the structure of one of the molecules. The three-coordinate Pd(I) complex has a P–Pd–P angle of $92.20(2)^{\circ}$ and two unequal P–Pd–N angles of $108.06(6)^{\circ}$ and $154.04(6)^{\circ}$. While the sum of the three angles (354.3°) indicates an idealized planar geometry for the Pd center, the presence of two unequal P–Pd–N angles differentiates **1** from trigonal-planar three-coordinate Pd(0) complexes ($\text{Pr}^i_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPr}^i_2$)Pd(PCy₃) (**29**) and Pd(PPh₃)₃ (**30**) and T-shaped three-coordinate Pd(II) complexes (P^tBu_3)Pd(C₆H₄-4-OCH₃)(N(C₆H₃-3,5-(CF₃)₂)₂) (**31**) and (IPr)Pd(3-methylnorborn-2-yl)(NHC₆H₄-4-CH₃) (IPr = 1,3-bis(2',6'-diisopropylphenyl)imidazole-2-ylidene) (**32**). The Pd–N bond distance in **1** is 2.063(2) Å, which is slightly longer than those of the three-coordinate Pd(II) amido complexes (sIPr)Pd(3-methylnorborn-2-yl)(NHC₆H₄-4-OCH₃) (sIPr = 1,3-bis(2',6'-diisopropylphenyl)imidazolin-2-ylidene) (2.037(3) Å) and (IPr)Pd(3-methylnorborn-2-yl)(NHC₆H₄-4-CH₃) (2.011(3) Å) (**32**). Counter to the knowledge that the *trans* influence of the amido ligand would elongate the *transoid* Pd–P bond, the 2.2883(7) Å Pd1–P2 bond is shorter than the 2.3314(7) Å Pd1–P1 bond. The shortening of the Pd–P bond distance might be caused by attractive dispersion forces between the phenyl groups on the P atom and the proximal 2,4,6-triisopropylphenyl group on the amido ligand (*vide infra*). In addition, the bond distances within the amido ligand of **1** itself are typical of anilido ligands in metal complexes (**31**, **32**), and are different from those of the parent phenylaminy radical [NHPh][•] (**33**) and the arylaminy complexes (**34-37**) (Table S1), which hints at the monoanionic nature of [NHAr^{Tri}]¹⁻ in **1**.

Spectroscopic and Electronic Structure Features of [(BINAP)Pd(NHAr^{Tri})]. Complex **1** features an $S = \frac{1}{2}$ ground spin-state as indicated by the measured magnetic moment of 2.1(1) μ_B .

Continuous wave (CW) and field-swept echo-detected (FSE) EPR were obtained for **1** (Figs. 3A-3C, and S73). The X-band (9 GHz) CW-EPR spectrum obtained at room temperature shows a four-line pattern centered at g_{iso} *ca.* 2.052 with $A_{iso}(^{31}\text{P1}) = 202$ G (567 MHz) and $A_{iso}(^{31}\text{P2}) = 80$ G (225 MHz) (Fig. S73). The anisotropy of the g -values and the ^{31}P A -values were resolved at low temperatures by obtaining spectra at X-, Q-, (35 GHz), and W-band (94 GHz). Figs. 3A-3C shows the frozen-solution multifrequency EPR spectra obtained for **1** along with simulations using globally-fit spin Hamiltonian parameters. The g -values obtained are $g_1 = 2.0085$, $g_2 = 2.0350$, and $g_3 = 2.1115$. The small g -value is consistent with the DFT-calculated electronic structure, as discussed below (Table 2), but its deviation from g_e (2.002) is unusual among the few known Pd(I) complexes. For example, the spectra of the Pd(I) species generated by γ -ray irradiation on Pd(II) compounds have their $g_{\perp}$ values in the range 2.0 to 2.1 and $g_{\parallel}$ values in the range 2.1 to 2.6 (38), the spectrum of $[(\text{PBU}'_3)_2\text{Pd}][\text{CB}_{11}\text{Cl}_{11}\text{H}]$ has the g -values of $g_{\perp} = 2.338$, $g_{\parallel} = 1.971$ (19), and that of $[(\text{PBU}'_3)_2\text{Pd}(\text{NCMe})][\text{CB}_{11}\text{Cl}_{11}\text{H}]$ shows $g_{\perp} = 2.088$, $g_{\parallel} = 2.314$ (19). The ^{31}P hyperfine constant values (HFCs) determined by globally fitting the frozen-solution EPR spectra of **1** for $^{31}\text{P1}$ are: $A_1 = 535$, $A_2 = 535$, and $A_3 = 631$ MHz. The values for $^{31}\text{P2}$ are $A_1 = 205$, $A_2 = 210$, and $A_3 = 260$ MHz. Deduction of atomic spin density from the isotropic (A_{iso}) and dipolar (T) contributions to the HFCs (39) yields a spin density of 13.0 % on P1, of which 4.3 % resides in the 3s orbital and 8.7 % in a 3p orbital, and a spin density on P2 is 6.4 %, where 1.7 % resides in the 3s orbital and 4.7 % in the 3p orbital. Thus, total spin density on two P nuclei is *ca.* 20 % based on the EPR experiments. $A(^{105}\text{Pd})$ and $A(^{14}\text{N})$ contributions to the spectra could not be resolved.

Fig. 3. Spectroscopic data of Pd complexes. (A-C) EPR spectra of **1** (black line) and simulations (red line) at 9 GHz CW, 34 GHz electron spin echo fieldsweep (derivative), and 94 GHz CW EPR. (D) Overlay of the smoothed second derivatives of Pd K-edge XAS spectra of $\text{Pd}^0(\text{IPr})_2$ (**5**, blue), **1** (red), and $(\text{BINAP})\text{Pd}^{\text{II}}(\text{OAc})_2$ (**6**, black). (E) Experimental (red) and

TDDFT calculated (black) Pd L₃-edge XAS spectra of **1**. The B3LYP functional and SARC-ZORA basis set was used for Pd, with ZORA-def2-TZVP(-f) used for all other atoms. Contributions of individual orbitals were obtained from Löwdin population analysis of the QROs. Orbitals are plotted at an isovalue of 0.03 au with hydrogen atoms removed for clarity.

Table 1. Experimental Pd K-Edge and L_{2,3}-Edge Energies.

Compound	K-edge (eV)	L ₃ pre-edge max (eV)	L ₂ pre-edge max (eV)	Total L ₃ + L ₂ Mainline Area
Pd ⁰ (IPr) ₂ (5)	24347	nd	nd	nd
(BINAP)Pd ^I (Ar ^{Trip}) (1)	24351	3174.5	3331.7	1.66(0.03)
(BINAP)Pd ^{II} (OAc) ₂ (6)	24353	3176.4	3333.6	4.02(0.16)

To probe the electronics of the Pd center in **1**, Pd K- and L-edge XAS data for **1**, the Pd(0) complex [Pd⁰(IPr)₂] (**5**), and the Pd(II) complex [(BINAP)Pd^{II}(OAc)₂] (**6**) were collected. As shown in Figs. S74 and 3D, and Table 1, the rising-edge energies obtained from K-edge (1s → valence/continuum) for the series of compounds shift toward higher energies with increasing formal oxidation state, though it has been noted that factors such as coordination environment and ligand identity can shift rising-edge energies to degrees similar to shifts caused by oxidation state changes (40). Pre-edge features arising from the metal 1s → *nd* transitions are also conventionally used to assess physical oxidation states. Such excitations are not expected for the Pd(0) complexes because of their *d*¹⁰ configuration, but will occur in the case of formally Pd(I) and Pd(II) complexes. Such features are not resolved in the experimental Pd K-edge spectra likely owing to the weak intensity of these quadrupole allowed but dipole forbidden transitions as well as the core-hole lifetime broadening endemic to 2nd and 3rd row metal K-edge XAS.

To complement the K-edge data, the Pd L_{2,3}-edge (2p → valence/continuum) XAS data were obtained, where dipole-allowed Pd 2p → 4d transitions gives rise to intense features that probe the energetics and covalency of the Pd ligand field (41). Experimental Pd L_{2,3}-edge spectra are shown in Figs. 3E and S75-S77 for **1** and **6**. L₃ and L₂ mainlines in these spectra can be assigned to excitations from the Pd 2p orbitals into singly or unoccupied Pd 4d orbitals. Satellite features at higher energies relative to the mainline result from transitions into higher lying levels of primarily ligand character (*vide infra*). The L₃ and L₂ mainlines for **1** are shifted by *ca.* 2 eV to lower energy relative to **6** (Table 1). Areas of L_{2,3}-edge mainlines can be used to quantify metal *nd* character in valence acceptor orbitals, providing a direct probe of covalency and physical oxidation state (40). This approach has been applied to Pd L_{2,3}-edges, where an increase in the L_{2,3}-edge area of PdAl₃ and PdCl₂ compared to Pd metal was attributed to *d*-count depletion (42). In the present case, the total L_{2,3}-edge mainline area of **1** is *ca.* half that of **6**, consistent with Pd-localized reduction.

Hybrid density functional theory (DFT) calculations were carried out to interrogate the electronic structure of **1**. All calculations used the dispersion-corrected B3LYP-D3 hybrid density functional (43) (44) with the segmented all-electron relativistically contracted (SARC)-ZORA basis on Pd (45) and ZORA-def2-TZVP(-f) basis set on all other atoms. All calculations used crystallographic coordinates.

Table 2. Experimental and DFT-calculated EPR parameters for **1**.

Experimental	Calculated ^a
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g tensor	[2.0085, 2.0350, 2.1115]	[2.0216, 2.0408, 2.1065]
$A(^{31}\text{P1})$ / MHz	[205, 210, 260]	[237, 242, 298]
$A(^{31}\text{P2})$ / MHz	[535, 535, 631]	[535, 537, 650]
$A(^{105}\text{Pd})$ / MHz	NR	[105, 31.1, 80.8]
$A(^{14}\text{N})$ / MHz	NR	[2.6, 3.3, 24.7]

^aCalculations used crystallographic coordinates with the B3LYP hybrid density function, D3 correction for dispersion, the SARC-ZORA basis set on Pd, and the ZORA-def2-TZVP(-f) basis set on all other atoms.

Veracity of the electronic structure calculations was judged by comparison of calculated spectroscopic parameters to experiment. Spin-Hamiltonian parameters calculated for **1** agree well with experiment (Table 2). Specifically, the *g*-values as well as the magnitudes and asymmetry of the ^{31}P HFCs are effectively reproduced by experiment. Calculated Mulliken spin densities comprise 9.5 % 3p and 3.9 % 3s on P1 and 5.7 % 3p and 2.7 % 3s on P2, in splendid agreement with analysis of the experimentally-obtained HFCs (*vide supra*). The calculation yielded low ^{14}N and ^{105}Pd HFC values, consistent with the fact that these features are unresolved in the EPR data.

The single-point DFT solutions were used as starting points for time-dependent DFT (TDDFT) calculations of the XAS data obtained for **1** and **6**. TDDFT has been used previously to calculate $\text{L}_{2,3}$ -edge XAS spectra for second-row transition metals and was shown to adequately reproduce the structure of experimental L_3 -edges without including the contributions from spin-orbit coupling that yield the L_3 - L_2 splitting (46). TDDFT reproduced the overall envelope of L_3 features in the experimental spectra (Figs. 3E and S79). The satellite features to higher energy of the L_3 mainlines comprise transitions into ligand-localized molecular orbitals with minimal Pd $4d$ character. The mainline transition in **1** primarily comprises the Pd $2p \rightarrow \text{SOMO}$ excitation, while for $(\text{BINAP})\text{Pd}^{\text{II}}(\text{OAc})_2$ the mainline consisted of the Pd $2p$ LUMO excitation as well as transitions to two additional low-lying MOs with ca. 10% contributions from Pd $4d$ orbitals. Calculated total Pd $4d$ character in all acceptor orbital holes against summed L_3 and L_2 mainline areas gives a correlation with $R^2 = 0.97$ (Fig. S81). Formally Pd^{I} complex **1** exhibits 30% lower overall d vacancy than the Pd^{II} complex, providing further support for metal-centered reduction relative to formally Pd^{II} -containing **6**.

The experimentally-validated DFT calculations indicate that **1** bears a three-electron two-center Pd–N π -bond, and its electronic configuration of can be described as $(\pi_{d_{xy}+p_N})^2(d_{z2}, d_{xz}, d_{z2}, d_{x2-y2})^8(\pi^*_{d_{xy}-p_N})^1$. Löwdin orbital populations show that the SOMO is highly delocalized, although there is a substantial (40%) Pd $4d$ contribution consistent with the observed anisotropy in *g*-values obtained for **1** (Fig. 4A). Major contributors to the SOMO come from the P-donors (10.3 % 3p) and the amide (10.4 % N 2p). The sum of the spin density on the $\text{NHAr}^{\text{Trip}}$ fragment, 0.22, precludes description of **1** as an aminyl radical complex. Relevant comparisons include the aminyl radical species $[(\text{bipy})\text{Rh}(\text{N}(\text{Trop})_2)][\text{OTf}]$ (0.56, bipy = bipyridine, Trop = 5*H*-dibenzo[*a,d*]cyclohepten-5-yl) (26), $[(\text{Ph}_2\text{B}(\text{CH}_2\text{P}^i\text{Bu}_2)_2)\text{Cu}(\text{N}(\text{tolyl-}p)_2)]$ (0.69) (36), $[(\text{Me}_3\text{NN})\text{Cu}(\text{NPh}_2)]$ (0.58, Me_3NN = 2,4-bis(2,4,6-trimethylphenylimido)pentyl) (37), $[(\text{PNP})\text{NiCl}][\text{OTf}]$ (0.69) (35), and $[(\text{PNP})\text{Re}(\text{CO})_3][\text{OTf}]$ (0.83) (34) that feature higher spin density on their N-ligands. To gain insight into the nature of the Pd–N bond in **1** and its unusual

stability, we further did bonding analysis by using the state-of-the-art energy decomposition analysis (EDA) (47) with the natural orbitals for chemical valency (NOCV) approach (48-50) (see SI for details). The most important numerical results are provided in Figure 4B, while the more detailed information can be found in Table S3 and Figs. S83-S87. The interacting neutral fragments of (BINAP)Pd⁰ and NHA^{Tri}p has comparable orbital energy (i.e., $\Delta E_{\text{orb}} = -72.0$ kcal/mol) with that of the ionic fragments of [(BINAP)Pd^I]⁺ and [NHA^{Tri}p]⁻ (i.e., $\Delta E_{\text{orb}} = -73.7$ kcal/mol), implying the two resonant structures exist for the complex **1** but the neutral fragments are slightly favored because of the smaller orbital energy (see Figure S87a). This also agrees very well with the spectroscopic data and spin density analysis as shown in Figure S83b. It revealed that there is significant Pauli repulsion (i.e., $\Delta E_{\text{Pauli}} = 123.1$ kcal/mol) within the Pd–N interaction by using the neutral interacting fragments. Nonetheless, the favorable attractive interactions, including the electrostatic energy ($\Delta E_{\text{elstat}} = -92.3$ kcal/mol) and orbital interaction energy ($\Delta E_{\text{orb}} = -72.0$ kcal/mol), can compensate and even exceeds the Pauli repulsion ΔE_{Pauli} by 41.2 kcal/mol. It should be emphasized that the dispersion energy (i.e., $\Delta E_{\text{disp}} = -31.3$ kcal/mol), contributing 16% of total attractive forces, leads to a summed bond dissociation energy (D_e) of 50.9 kcal/mol—help to stabilize the Pd(I) amido species at ambient temperature. The dispersion forces can be discerned from the short inter-ligand H•••H contacts between BINAP and NHA^{Tri}p in the optimized structure of **1** (Fig. 4C). The ionic interacting fragments has similar Pauli repulsion and orbital energies but with a significant strong electrostatic energy ($\Delta E_{\text{elstat}} = -163.5$ kcal/mol), which is understandable between the cation [(BINAP)Pd^I]⁺ and anion [NHA^{Tri}p]⁻ fragments and thus leads to more larger intrinsic energy ΔE_{int} of -139.0 kcal/mol and bond dissociation energy (D_e) of 121.3 kcal/mol.

Fig. 4. DFT calculations of Pd(I) amido complex. (A) Selected molecular orbitals of **1**, hydrogen atoms on ligands were omitted. (B) EDA-NOCV results (in kcal/mol). Fragments of

(BINAP)Pd and $\text{NHAr}^{\text{Trip}}$ are given on table in singlet (S) or doublet (D) electronic states. (C) Short inter-ligand $\text{H}\cdots\text{H}$ contacts with the distances less than 2.4 Å (purple lines).

Reactivity of $[(\text{BINAP})\text{Pd}(\text{NHAr}^{\text{Trip}})]$. Complex **1** is the first isolable d^9 platinum-group-metal complex bearing a π -donating ligand. Being different from the aforementioned fleeting Pd(I) species, it is stable at ambient temperature, which facilitates studies of its reactivity. When **1** is subjected to thermolysis, light-irradiation, or coordination with exogenous ligands, it undergoes Pd–N bond homolytic cleavage reactions to yield anilines and Pd(0) species (Fig. 5A). In these reactions, the arylaminyl radical dimerization product **2**, the alkane-chain dehydrogenation product **3** and the aniline $\text{NH}_2\text{Ar}^{\text{Trip}}$ (**4**) are observed, implicating the radical intermediate $[\text{NHAr}^{\text{Trip}}]^{\bullet}$ in these reactions (Fig. S19). In addition, two Pd(0) complexes, $[(\text{BINAP})\text{Pd}(2,6\text{-(CH}_3)_2\text{-C}_6\text{H}_3\text{NC})_2]$ (**7**) and $[(\text{BINAP})\text{Pd}(\eta^2\text{-3,5-(CF}_3)_2\text{-C}_6\text{H}_3\text{CH=CH}_2)]$ (**8**), have been isolated in the corresponding reaction and structurally authenticated by X-ray diffraction studies (Figs. S29 and S34). The decomposition reaction of **1** under white light-irradiation (6 W LED) at room temperature shows zero-order kinetics with a kinetic constant $k_{\text{irri}} = 1.6 \times 10^{-8} \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$ (Fig. S23), whereas the thermal decomposition reaction at 348 K is a first-order reaction with a rate constant $k_{\text{therm}} = 1.1 \times 10^{-4} \text{ s}^{-1}$ (Fig. S27). The thermal and light-irradiation-induced decomposition reactions of **1** might result from amido-to-palladium(I) electron-transfer to form $(\text{BINAP})\text{Pd}^0(\text{NHAr}^{\text{Trip}})^{\bullet}$. The absorption spectrum of **1** in toluene shows an intense feature at 808 nm ($7300 \text{ mol}^{-1}\cdot\text{L}\cdot\text{cm}^{-1}$). TDDFT calculations suggest that the band principally arises due to a charge transfer (CT) transition comprising transfer of an electron from the nitrogen lone-pair on $[\text{NHAr}^{\text{Trip}}]^{-1}$ and from Pd $4d_{z^2}$ to the SOMO of **1** (Fig. S78). Either transition fully populates the Pd–N antibonding MO and thus promotes bond cleavage. Kinetics obtained under pseudo-first-order conditions involving both the concentrations of **1** and the alkene 3,5-bis(trifluoromethyl)styrene of the ligand-coordination-induced-decomposition reactions of **1** with an excess amount of 3,5-bis(trifluoromethyl)styrene in benzene at 30 °C suggest an associative mechanism (Figs. S41–S47).

Fig. 5. Reactivity of 1. (A) Thermolysis-, light irradiation, and ligand-coordination-induced decomposition reactions of **1**, as well as its reactions with primary amines and a phenol. (B) The Hammett plot with *para*-substituted 2,6-dimethylaniline (k_X/k_H = relative rate constants for *para*-X substituted 2,6-dimethylanilines versus 2,6-dimethylaniline; σ_p = Hammett substituent constant, ρ = reaction constant). (C) The kinetic isotope effect k_H/k_D for the reactions of **1** with 2,6-dimethylaniline.

The amido ligand in **1** is highly basic in accord with the severe Pauli repulsion in the Pd–N π -bonding. When **1** is treated with phenols and amines, *e.g.* 2,6-di(*tert*-butyl)-4-methylphenol, 2,6-di(*isopropyl*)aniline, 2,6-dimethylaniline, *n*-butyl amine, and *n*-octyl amine, the free aniline $\text{NH}_2\text{Ar}^{\text{Trip}}$ (**4**) was formed in high yields. The reaction with the phenol allows the isolation of a Pd(0) complex (2,6-di-*tert*-butyl-4-methylenecyclohexa-2,5-dienone)palladium(0) complex (**9**) in 67% yield (Fig. 5A), whose structure has been confirmed by X-ray diffraction (Figs. S48 and S49). The reactions with amines produced blue-purple mixtures and the attempts to isolate palladium-containing species from the mixture were unsuccessful. These reactions likely start with a proton-transfer step between the basic amido ligand in **1** and the H–X (X = O, N) bonds in phenols and amines, rather than a hydrogen-atom-abstraction mechanism as i) a linear Hammett plot with a positive reaction constant $\rho = +0.77$ was obtained for the reactions of **1** with anilines bearing different *para*-substituents (Fig. 5B), ii) no obvious kinetic isotope effect was observed in the reactions **1** with 2,6-Me₂C₆H₃NH₂ and 2,6-Me₂C₆H₃ND₂ (Fig. 5C), iii) no reaction took place when **1** was treated with substrates bearing weak C–H bonds, *e.g.* xanthene (73.3 kcal/mol in DMSO) and cyclohexa-1,4-diene (67 kcal/mol in gas phase), whose C–H bond dissociation energies are much lower than those of the O–H bond of 2,6-di(*tert*-butyl)-4-methylphenol (78 kcal/mol in DMSO) and the N–H bonds of amines (≥ 89 kcal/mol in DMSO) (51). Thus, the formation of the Pd(0) complex **9** can be explained by the sequential steps of proton-transfer followed by electron-transfer and hydrogen-atom abstraction reactions (Fig. S55). Notably, as anilido anions are generally less basic than aliphatic amido anions (51), the capability of **1** to react with the aliphatic amines has well-demonstrated the super-basicity of its amido ligand, which is a consequence of Pauli repulsion in the 4d⁹ metal amido complex.

In summary, the first isolable, room-temperature stable Pd(I) complex bearing an π -donating ligand [(BINAP)Pd(NHAr^{Trip})], which also represents the first platinum-group-metal amido complex with a nd^9 electronic configuration, has been synthesized from the salt elimination reaction of (BINAP)PdCl₂ with LiNHAr^{Trip}. The Pd(I) amido complex features a long Pd–N bond and inequivalent N–Pd–P angles. EPR and XAS spectroscopies indicate that Pd–N bond in the Pd(I) amido complex is highly covalent. Theoretical studies accord with the spectroscopic data and further revealed that pronounced dispersion forces between the BINAP and the bulky amido ligand NHAr^{Trip} are likely responsible for the unusual stability of this complex. Reactivity studies revealed that the Pd–N bond in [(BINAP)Pd(NHAr^{Trip})] can undergo homolytic cleavage reaction to release the aminyl radical [NHAr^{Trip}][•] when the complex is subjected to heat, light-irradiation, or ligand-coordination. As a consequence of the severe Pauli repulsion, the anilido ligand in the Pd(I) complex exhibits strong basicity, and can even deprotonate aliphatic amines. The reactivity profile of the Pd(I) amido complex points out the potential synthetic utility of low-valent platinum-group-metal species bearing π -donating ligands for the design of new reactions.

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Supplementary Materials:

Materials and Methods

Figures S1-S86

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Tables S1-S3

References (52-83)

Data S1

Supplementary Materials for

An Isolable Mononuclear Palladium(I) Amido Complex

Jian Liu¹, Melissa M. Bollmeyer², Yujeong Kim^{3,4}, Dengmengfei Xiao⁵, Samantha N. MacMillan², Qi Chen¹, Xuebing Leng¹, Sun Hee Kim^{3,4*}, Lili Zhao^{5*}, Kyle M. Lancaster^{2*}, and Liang Deng^{1*}

*Corresponding author. Email: shkim7@kbsi.re.kr (S.H.K), ias_llzhao@njtech.edu.cn (L.Z.), kml236@cornell.edu (K.M.L.), deng@sioc.ac.cn (L.D.).

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Materials and Methods

General Procedures. All experiments were performed either under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk techniques or in a glovebox. Organic solvents were dried with a solvent purification system (Innovative Technology) and bubbled with dry N₂ gas prior to use. (BINAP)PdCl₂ (BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthalene) (52), LiNHAr^{Trip} (Ar^{Trip} = 2,6-bis(2',4',6'-triisopropylphenyl)phenyl) (53), *N,N'*-dideuterium-2,6-dimethylaniline (54), and Pd(IPr)₂ (55) were synthesized according to literature procedures. Chemicals were purchased from chemical vendors and used as received unless otherwise noted. ¹H, ¹³C, ¹⁹F, and ³¹P NMR spectra were recorded with Agilent 400 MHz or Bruker 400 MHz or JEOL 600MHz NMR spectrometer. All chemical shifts were reported in units of ppm with references to the residue of the deuterated solvents for proton and carbon chemical shifts, to external 85% phosphoric acid solution for phosphorous chemical shifts, to CF₃COOH for fluorine chemical shifts, and to CDCl₃ for deuterium chemical shifts. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS). Magnetic moments were measured by the method originally described by Evans with stock and experimental solutions containing a known amount of a (CH₃)₃SiOSi(CH₃)₃ standard (56). Absorption spectra were recorded with a Shimadzu UV-3600 UV-vis-NIR spectrophotometer. IR spectra were recorded with NICOLET AVATAR 330 FT-IR spectrophotometer and Bruker ALPHA II Sample Compartment RT-DLaTGS. The photoreactors used in this research were bought from GeAo Chem (white LEDs, luminous flux ≥ 110 lm, beam angle = 120 °, current intensity ≥ 350 mA, 1 W for every light bulb; every Schlenk tube was irradiated by 6 light bulbs from the side).

Synthesis and Characterization of [(BINAP)Pd(NHAr^{Trip})] (**1**)

Preparation of [(BINAP)Pd(NHAr^{Trip})] (1**).** To an orange suspension of (BINAP)PdCl₂ (200 mg, 0.25 mmol) in toluene (20 mL) was added LiNHAr^{Trip} (277 mg, 0.55 mmol) at -78 °C. The color of the reaction mixture changed to blue immediately. The mixture was slowly warmed to room temperature and then kept stirring for 2 h. During the course, the color of the reaction mixture changed to green gradually. The resultant mixture was filtered through diatomaceous earth, and the filtrate was concentrated under vacuum to leave a green residue. The residue was dissolved by diethyl ether (5 mL). The ether solution was concentrated and kept at -30 °C for days to yield green crystals. The green crystals were collected by filtration, and a single-crystal X-ray diffraction study confirmed its identity as the palladium(I) amido complex **1** (156 mg, 51%). After collecting of **1** by filtration, the filtrate was concentrated under vacuum to leave a residue. The residue was dissolved in C₆D₆ (500 μ L) and 1,3,5-trimethoxybenzene (2.5 mg, 0.015 mmol) was added as an internal standard for NMR quantification, which indicates the NMR yields of **2**, **3** and **4** in 66%, 6% and 18%, respectively (Fig. S8.). The isolation and characterization of **2**, **3** and **4** can be independently achieved (*vide infra*). For [(BINAP)Pd(NHAr^{Trip})] (**1**): Anal. Calcd for C₈₀H₈₂P₂PdN: C, 78.38; H, 6.74; N, 1.14; Found: C, 78.58; H, 6.97; N, 1.18. Magnetic susceptibility (C₆D₆, 294 K): $\mu_{\text{eff}} = 2.1(1) \mu_{\text{B}}$. Absorption spectrum (toluene): λ_{max} , nm (ϵ , M⁻¹ cm⁻¹) = 300 (12000), 390 (6000), 800 (7300). IR (KBr, cm⁻¹): ν = 3478 (w), 3379 (w), 3303 (w), 3051 (m), 2957 (s), 2925 (s), 2864 (m), 1605 (m), 1575 (m), 1459 (m), 1435(s), 1398 (m), 1380 (m), 1360 (m), 1311 (m), 1098 (m), 1071 (m), 876 (m), 814 (m), 745 (s), 696 (s), 523 (m), 504 (s).

Fig. S1. Molecular structure of **1a**, showing one of the two crystallographically independent molecules in the unit cell with 30% probability ellipsoids and the partial atoms numbering scheme. Hydrogen atoms, except the one on N1, are omitted for clarity. Selected distances (Å) and angles (deg): Pd1-N1 2.063(2), Pd1-P1 2.3314(7), Pd1-P2 2.2883(7), N1-C45 1.377(3), P2-Pd1-P1 92.20(2), N1-Pd1-P1 108.06(6), N1-Pd1-P2 154.04(6), Pd1-N1-H1 112.4, C45-N1-Pd1 135.29(18), C45-N1-H1 112.3.

Fig. S2. Molecular structure of **1b**, showing another one of the two crystallographically independent molecules in the unit cell with 30% probability ellipsoids and the partial atoms numbering scheme. Hydrogen atoms, except the one on N2, are omitted for clarity. Selected distances (Å) and angles (deg): Pd2-N2 2.063(2), Pd2-P3 2.3211(7), Pd2-P4 2.2841(7), N2-C125 1.371(3), P3-Pd2-P4 92.04(2), N2-Pd2-P3 114.39(6), N2-Pd2-P4 149.54(6), Pd2-N2-H2 110.0, C125-N2-Pd2 139.98(18), C125-N2-H2 110.0.

Fig. S3. UV-vis absorption spectrum in toluene of **1** recorded at room temperature.

Fig. S4. IR spectrum of **1**.

Fig. S5. Comparison of IR spectra of $[(\text{BINAP})\text{Pd}(\text{NHAr}^{\text{Trip}})]$ (**1**, red line) and $[(\text{BINAP})\text{Pd}(\text{NDAr}^{\text{Trip}})]$ (**1-d**, blue line) (3484 cm^{-1} is the characteristic peak of N-H bond, 2641 cm^{-1} is the characteristic peak of N-D bond).

Fig. S6. Mass spectrum of **1** (top) and its simulated spectrum (bottom).

Fig. S7. Mass spectrum of $[(\text{BINAP})\text{Pd}(\text{NDAr}^{\text{Trip}})]$ (**1-d**, top) and its simulated spectrum (bottom).

Fig. S8. The ^1H NMR spectrum of the mixture of **2**, **3** and **4** formed in the preparation of **1**.

Isolation and Characterization of 2. To an orange suspension of (BINAP)PdCl₂ (200 mg, 0.25 mmol) in toluene (20 mL) was added LiNHAr^{Trip} (277 mg, 0.55 mmol) at -78 °C. The reaction mixture was then warmed to room temperature and kept stirring for 2 h. The resultant mixture was filtered through diatomaceous earth, and the filtrate was concentrated under vacuum to leave a green residue. The residue was extracted with *n*-hexane (5 mL x 3), and the *n*-hexane solution was combined and concentrated. Standing the *n*-hexane solution at room temperature afforded **2** as white crystals (49 mg, 39%). For **2**: ¹H NMR (400 MHz, C₆D₆, 296 K): δ (ppm) 9.42 (s, 1H), 7.14-7.02 (m, 10H), 6.88 (t, *J* = 7.5 Hz, 1H), 5.80 (s, 1H), 5.51 (s, 1H), 4.67 (s, 1H), 3.64 (d, *J* = 8.2 Hz, 1H), 3.17-2.69 (m, 12H), 1.39 (d, *J* = 6.8 Hz, 3H), 1.32 (d, *J* = 6.9 Hz, 3H), 1.28-1.20 (m, 30H), 1.18-1.03 (m, 36H). ¹³C NMR (101 MHz, C₆D₆, 296 K): δ (ppm) 166.34, 149.30, 149.01, 147.88, 147.73, 147.64, 147.38, 147.28, 146.58, 146.38, 145.90, 139.02, 138.96, 137.44, 136.21, 134.86, 133.99, 131.81, 131.29, 130.48, 121.90, 121.88, 121.20, 121.16, 120.91, 120.39, 120.26, 56.38, 34.80, 34.73, 34.57, 31.46, 31.27, 31.25, 31.05, 30.87, 25.97, 25.92, 25.10, 24.99, 24.79, 24.67, 24.55, 24.40, 24.37, 24.28, 24.26, 24.22, 24.17, 24.14, 24.07, 23.09, 23.07. HRMS (ESI): calcd for C₇₂H₁₀₁N₂ [(M+H)⁺], 993.7959; Found, 993.7941. IR (thin film, cm⁻¹): ν = 3341 (m), 2960 (s), 2976 (s), 2867 (s), 1765 (w), 1656 (m), 1606 (m), 1564 (s), 1461 (s), 1433 (s), 1414 (s), 1382 (m), 1361 (m), 1325 (m), 1266 (m), 1248 (m), 1229 (m), 1170 (m), 1103 (m), 1077 (m), 1054 (m), 1001 (m), 955 (m), 942 (m), 919 (m), 877 (m), 858 (m), 804 (m), 765 (m), 713 (m), 651 (m), 582 (w), 563 (w), 487 (w).

Fig. S9. Molecular structure of **2**, showing 30% probability ellipsoids and the partial atoms numbering scheme, hydrogen atoms were omitted (except on N). Selected distances (Å) and angles (deg) of **2**: N1-C1 1.287(3), C1-C2 1.487(3), C2-C3 1.335(3), C3-C4 1.489(3), C5-C4 1.487(3), C5-C6 1.334(3), C1-C6 1.482(3), N2-C4 1.481(3), N2-C37 1.415(3), C37-C38 1.417(3), C38-C39 1.388(3), C39-C40 1.385(4), C40-C41 1.376(4), C41-C42 1.393(3), C42-C37 1.405(3).

Fig. S10. ¹H NMR spectrum of **2** (Inset: expanded region of ¹H NMR spectrum of **2** from 1.42 to 1.0 ppm).

Fig. S11. ^{13}C NMR spectrum of **2** (Inset: expanded region of ^{13}C NMR spectrum of **2** from 35.0 to 21.0 ppm).

Fig. S12. IR spectrum of **2**.

Isolation and Characterization of 3 and 4. To an orange suspension of (BINAP)PdCl₂ (800 mg, 1.00 mmol) in toluene (80 mL) was added LiNHAr^{Trip} (1117 mg, 2.20 mmol) at -78 °C. The reaction mixture was then warmed to room temperature and kept stirring for 2 h. The resultant mixture was filtered through diatomaceous earth, and the filtrate was concentrated under vacuum to leave a green residue. The residue was extracted with *n*-hexane (5 mL x 3), and the *n*-hexane solution was combined and concentrated under vacuum to leave a residue. The residue was purified by flash column chromatography (silica gel, *n*-hexane as elute) to give **3** and **4** as white solid. For **3**: 20 mg, 4%. ¹H NMR (400 MHz, C₆D₆, 296 K): δ (ppm) 7.32-7.20 (m, 4H), 7.07-6.96 (m, 2H), 6.79 (t, *J* = 7.5 Hz, 1H), 5.02 (s, 2H), 3.18-2.77 (m, 7H), 1.88 (s, 3H), 1.36-1.14 (m, 30H). ¹³C NMR (101 MHz, C₆D₆, 296 K): δ (ppm) 148.86, 148.62, 148.44, 148.26, 148.02, 147.47, 145.04, 142.87, 133.92, 133.06, 130.31, 129.76, 125.62, 125.33, 124.86, 122.89, 121.53, 121.44, 117.63, 114.88, 34.85, 34.56, 31.00, 30.71, 30.43, 24.96, 24.71, 24.47, 24.40, 24.29, 24.25, 24.10, 24.05. HRMS (ESI): calcd for C₃₆H₅₀N [(M+H)⁺], 496.3938; Found, 496.3939. IR (thin film, cm⁻¹): ν = 3476 (w), 3380 (w), 3049 (w), 2957 (s), 2923 (m), 2866 (m), 1600 (m), 1568(w), 1445 (m), 1365 (m), 1309 (w), 1258 (m), 1208 (w), 1168 (w), 1062 (m), 880 (m), 796 (m), 748 (m), 650 (w), 476 (w). For **4**: 263 mg, 53%. The isolated yield of **4** is higher than that of the NMR yield, which might be due to the decomposition of **2** during column chromatography. The latter reaction could also produce **4**. ¹H NMR (400 MHz, C₆D₆, 296 K): δ (ppm) 7.26 (s, 4H), 7.04 (d, *J* = 7.4 Hz, 2H), 6.83 (t, *J* = 7.4 Hz, 1H), 3.08-2.99 (m, 4H), 2.97 (s, 2H), 2.92-2.81 (m, 2H), 1.31-1.25 (m, 24H), 1.22 (d, *J* = 6.9 Hz, 12H) (Fig. S16.). The NMR data of **4** are identical to those reported in the literature (53).

Fig. S13. ¹H NMR spectrum of **3** (Inset: expanded region of ¹H NMR spectrum of **3** from 1.40 to 1.13 ppm).

Fig. S14. ¹³C NMR spectrum of **3** (Inset: expanded region of ¹³C NMR spectrum of **3** from 150.0 to 142.5 ppm and from 25.2 to 23.5 ppm).

Fig. S15. IR spectrum of **3**.

Fig. S16. ^1H NMR spectrum of **4** (Inset: expanded region of ^1H NMR spectrum of **4** from 1.35 to 1.15 ppm).

Equimolar Reaction of (BINAP)PdCl₂ with LiNHAr^{Trip}. To an orange suspension of (BINAP)PdCl₂ (640 mg, 0.8 mmol) in toluene (30 mL) was added LiNHAr^{Trip} (440 mg, 0.88 mmol) at -78 °C. The reaction mixture was then warmed to room temperature and kept stirring for 2 h. The mixture changed into a blue suspension that was filtered to afford a blue solid. The solid was then washed with toluene (3×2 mL) and dried under vacuum. The resultant solid is slightly soluble in C₆D₆. The ¹H NMR and ³¹P NMR analyses indicate the solid might contain (BINAP)PdCl(NHAr^{Trip}) (A) (Figs. S17 and S18). However, our attempts to isolate the desired complex upon recrystallization were unsuccessful.

Fig. S17. The ^1H NMR spectrum of the mixture formed from equimolar reaction of $(\text{BINAP})\text{PdCl}_2$ with $\text{LiNHAr}^{\text{Trip}}$ (Inset: expanded region of ^1H NMR spectrum of reaction mixture from 1.71 to 1.35 ppm).

Fig. S18. The ^{31}P NMR spectrum of the mixture formed from equimolar reaction of $(\text{BINAP})\text{PdCl}_2$ with $\text{LiNHAr}^{\text{Trip}}$.

Fig. S19. Possible route for the reaction of (BINAP)PdCl₂ with LiNDAr^{Trip}.

Table S1. Selected interatomic distances (Å) of the NHAr moieties in PhNH (**B**) (57), some metal anilido complex (**C**) (32) and the aminyl radical complexes **D-F** (34-36).

	N-C	C-C ^o	C ^o -C ^m	C ^m -C ^p
B	1.341	1.435/1.434	1.384/1.383	1.405/1.405
C	1.376(5)	1.404(5)/1.406(5)	1.389(5)/1.391(5)	1.389(6)/1.392(6)
D	1.382(3)	1.419(3)/1.409(3)	1.389(4)/1.386(4)	1.394(3)/1.393(3)
	1.390(3)	1.410(4)/1.416(3)	1.388(3)/1.391(3)	1.388(3)/1.399(4)
E	1.407(3)	1.406(3)/1.402(3)	1.391(3)/1.383(3)	1.398(3)/1.397(3)
	1.397(3)	1.403(3)/1.402(3)	1.382(3)/1.385(3)	1.398(3)/1.394(3)
F	1.391(3)	1.420(3)/1.408(4)	1.391(3)/1.381(3)	1.400(4)/1.400(3)
	1.401(3)	1.414(3)/1.403(4)	1.399(3)/1.386(3)	1.403(4)/1.403(3)
1	1.377(3)	1.431(4)/1.421(4)	1.391(4)/1.393(4)	1.379(4)/1.378(4)

Reactivity of [(BINAP)Pd(NHAr^{Trip})] (**1**)

Decomposition Reaction of **1 under White LED Irradiation.** White LED-irradiation on the C₆D₆ solution of **1** can induce its decomposition to yield **3** and **4** in comparable yields, along with diamagnetic palladium phosphine complexes as indicated by ¹H and ³¹P NMR spectra (Figs. S20 and S21). Adding dodecane as an internal standard, the yields of **3** and **4** were also confirmed by GC (Fig. S22.). The attempts to isolate the palladium-containing products were unsuccessful. Kinetic study on the decomposition reaction has been performed. The kinetic study monitors the increase of the characteristic ¹H NMR signal of **3** at $\delta = 5.02$ ppm formed in the reaction with 1,3,5-trimethoxybenzene as internal standard. The procedure is as following: To a J-Young tube were added **1** (15 mg, 0.010 mmol), 1,3,5-trimethoxybenzene (6.3 mg, 0.037 mmol) and C₆D₆ (500 μ L), then J-Young tube is illuminated by white LED (2 x 3 W white LEDs). The plot of yield vs time is shown in Fig. S23.

Fig. S20. ^1H NMR spectrum of the mixture formed from exposing the C_6D_6 solution of **1** under white LED for 90 h (Inset: expanded region of ^1H NMR spectrum of reaction mixture from 6.85 to 6.25 ppm).

Fig. S21. ^{31}P NMR spectrum of the mixture formed from exposing the C_6D_6 solution of **1** under white LED for 90 h.

Fig. S22. GC graph of the sample obtained from exposing the C₆D₆ solution of **1** under white LED for 90 h.

Fig. S23. Plot of yield of **3** (based on the full amount of $\text{NHAr}^{\text{Trip}}$ in **1**) versus time for the decomposition reaction of **1** under white LED at room temperature. In 90 h, the yield of **3** achieved 40% that suggests the conversion of **1** of 80% as merely half of the $\text{NHAr}^{\text{Trip}}$ is converted to **3**.

Decomposition of **1 under Thermolysis.** **1** is heat-sensitive. Its decomposition in C_6D_6 at 70 °C yields **3** and **4** in comparable yields, along with unidentified diamagnetic palladium phosphine species as indicated by ^1H and ^{31}P NMR spectra (Figs. S24 and S25). Adding dodecane as an internal standard, the yields of **3** and **4** were also confirmed by GC (Fig. S26.). The kinetic studies on the thermolysis-induced decomposition reaction of **1** monitor the increase of the characteristic ^1H NMR signal of **3** at $\delta = 5.02$ ppm formed in the reaction at 70 °C with 1,3,5-trimethoxybenzene as internal standard. The procedure is as following: To a J-Young tube was added **1** (10 mg, 0.008 mmol), 1,3,5-trimethoxybenzene (0.10 M in C_6D_6 , 100 μL). Then the reaction mixture was diluted with C_6D_6 to 500 μL . The mixture was warmed to 70 °C and monitored by ^1H NMR. The plot of yields of **3** versus time is shown in Fig. S27. By observing the change in half-life, the thermal decomposition reaction at 70 °C is a first-order reaction.

Fig. S24. ^1H NMR spectrum of the mixture formed from heating the C_6D_6 solution of **1** under 70 °C for 14 h (Inset: expanded region of ^1H NMR spectrum of reaction mixture from 6.85 to 6.25 ppm).

- 21.13

^{31}P NMR, 162 MHz, C_6D_6

Fig. S25. ^{31}P NMR spectrum of the mixture formed from heating the C_6D_6 solution of **1** under 70 °C for 14 h.

Fig. S26. GC graph of the sample obtained from heating the C_6D_6 solution of **1** under 70 °C for 14 h.

Fig. S27. Plot of yield of **3** (based on the full amount of NHAr^{Trip} in **1**) versus time for decomposition reaction of **1** under 70 °C. In 14 h, the yield of **3** achieved 40% that suggests the conversion of **1** of 80% as merely half of the NHAr^{Trip} is converted to **3**. The half-life is $t_{1/2} = 3.1$ h.

Reaction of 1 with 2,6-dimethylphenylisocyanide. To a solution of **1** (200 mg, 0.16 mmol) in toluene (20 mL) was added 2,6-dimethylphenylisocyanide (43 mg, 0.33 mmol) at room temperature. The color of the solution changed from green to red immediately. After stirring for 2 h, the red precipitate was collected by filtration. The resultant red solid was then washed with toluene (3×2 mL) and dried under vacuum, which leaves [(BINAP)Pd(2,6-(CH₃)₂C₆H₃NC)₂] (**7**) as a red powder (156 mg, 96%). Single crystals of **7** suitable for X-ray diffraction were grown by diffusion of a toluene solution of 2,6-dimethylphenylisocyanide into a concentrated toluene solution of **1** at -30 °C for days. Anal. Calcd for C₆₂H₅₀P₂PdN₂: C, 75.11; H, 5.08; N, 2.83; Found: C, 75.06; H, 5.45; N, 2.31. Absorption spectrum (THF): λ_{max}, nm (ε, M⁻¹ cm⁻¹) = 350 (8800), 520 (3500). IR (KBr, cm⁻¹): ν = 3048 (s), 3000 (m), 2944 (m), 2860 (w), 2062 (s), 2029 (s), 1841 (w), 1614 (w), 1587 (s), 1499 (m), 1468 (s), 1432 (s), 1379 (w), 1303 (m), 1186 (m), 1085 (s), 1027 (m), 812 (s), 774 (s), 741 (s), 502 (s), 457 (m). After the collection of **7** by filtration, the filtrate was concentrated under vacuum to leave a residue. The residue was dissolved in C₆D₆ (500 μL) and 1,3,5-trimethoxybenzene (12.1 mg, 0.072 mmol) was added as an internal standard for NMR quantification, which indicates the NMR yields of **2**, **3** and **4** in 44%, 5% and 39%, respectively (Fig. S28.).

Fig. S28. The ^1H NMR spectrum of the mixture formed from the reaction of **1** with two equiv. of 2,6-dimethylphenylisocyanide (Inset: expanded region of ^1H NMR spectrum of reaction mixture from 6.9 to 5.0 ppm).

Fig. S29. Molecular structure of **7**, showing 30% probability ellipsoids and the partial atoms numbering scheme. Selected distances (Å) and angles (deg): Pd-C1 2.004(3), Pd-P1 2.3493(8), N1-C1 1.156(4), C1-Pd-I 86.45(6), C1-Pd-P1 112.17(9), C1-Pd-P2 114.82(9), P1-Pd-P2 94.00(4), C2-Pd-P1 114.82(9), C2-Pd-P2 112.18(9).

Fig. S30. UV-vis absorption spectrum in THF of **7** recorded at room temperature.

Fig. S31. IR spectrum of **7**.

Reaction of 1 with 3,5-di(trifluoromethyl)styrene: To a solution of **1** (250 mg, 0.20 mmol) in toluene (20 mL) was added 3,5-di(trifluoromethyl)styrene (73 mg, 0.30 mmol) at room temperature. The color of the solution changed from green to yellow gradually. After stirring for 48 h, the mixture was concentrated under vacuum to leave a yellow residue. The resultant yellow solid was then washed with *n*-hexane (3×2 mL) and dried under vacuum, which leaves [(BINAP)Pd(η^2 -H₂C=CHC₆H₃-3,5-(CF₃)₂)] (**8**) as a yellow powder (180 mg, 91%). Single crystals of **8** suitable for X-ray diffraction were grown by diffusion of a *n*-hexane solution of 3,5-di(trifluoromethyl)styrene into a concentrated toluene solution of **1** at room temperature for days. Anal. Calcd for C₅₄H₃₈P₂PdF₆: C, 66.92; H, 3.95; Found: C, 66.93; H, 4.18. Absorption spectrum (THF): λ_{max} , nm (ϵ , M⁻¹ cm⁻¹) = 340 (12300), 400 (7400). IR (KBr, cm⁻¹): ν = 3053 (m), 2995 (w), 1604 (m), 1585 (m), 1497 (m), 1435 (m), 1394 (m), 1352 (w), 1306 (w), 1277 (s), 1220 (w), 1164 (s), 1128 (s), 1100 (m), 890 (m), 873 (m), 814 (w), 743 (s), 694 (s), 521 (m), 504 (s), 463 (m), 432 (w). The ¹⁹F and ³¹P NMR data indicate the presence of two isomers of **8** with the ratio of 1:2.4, probably related to the different orientation of the styrene ligand toward the (BINAP)Pd unit that has C₂-symmetry. ¹H NMR (400 MHz, C₆D₆, 296 K): δ (ppm) 8.15-8.03 (m), 7.84-7.75 (m), 7.52 (s), 7.48-7.35 (m), 7.33-7.18 (m), 7.15-7.07 (m), 7.05-6.91 (m), 6.84-6.76 (m), 6.74-6.67 (m), 6.65-6.56 (m), 6.47-6.40 (m), 6.39-6.30 (m), 6.27-6.20 (m), 4.80-4.68 (m), 4.59-4.45 (m), 3.65-3.52 (m), 3.50-3.39 (m), 3.22-3.13 (m), ¹³C NMR (101 MHz, C₆D₆, 296 K): δ (ppm) 150.03, 149.35, 149.33, 149.28, 149.26, 138.49, 138.46, 138.32, 138.05, 138.01, 137.90, 137.29, 137.20, 137.04, 136.96, 136.87, 136.68, 136.61, 136.39, 136.30, 136.06, 135.26, 135.09, 135.02, 134.92, 134.88, 134.84, 134.81, 134.78, 134.75, 134.70, 134.63, 134.54, 134.27, 134.25, 134.17, 134.12, 134.10, 134.05, 133.76, 133.59, 133.31, 133.24, 133.20, 132.49, 132.43, 132.20, 132.14, 131.77, 131.48, 131.40, 131.38, 131.16, 131.08, 131.06, 130.84, 130.06, 129.91, 129.87, 129.76, 129.37, 129.34, 128.87, 128.84, 128.77, 128.74, 128.67, 128.65, 128.63, 128.56, 128.50, 128.30, 127.93, 127.82, 127.67,

127.57, 127.54, 127.50, 127.45, 127.21, 127.15, 127.10, 127.04, 127.00, 126.95, 126.85, 126.05, 126.02, 125.97, 125.90, 125.84, 125.70, 124.29, 123.26, 123.13, 115.19, 67.23, 67.19, 67.02, 66.97, 63.38, 63.21, 46.72, 46.65, 45.46, 45.41, 45.21, 45.16. ^{31}P NMR (162 MHz, C_6D_6 , 296 K): δ (ppm) 30.01 (d, $J = 22.1$ Hz), 29.73 (d, $J = 23.0$ Hz), 25.10 (d, $J = 22.9$ Hz), 20.93 (d, $J = 22.1$ Hz). ^{19}F NMR (377 MHz, C_6D_6 , 296 K): δ (ppm) -62.39, -62.71. After the collection of **8** by filtration, the filtrate was concentrated under vacuum to leave a residue. The residue was dissolved in C_6D_6 (500 μL) and 1,3,5-trimethoxybenzene (28 mg, 0.17 mmol) was added as an internal standard for NMR quantification, which indicates the NMR yields of **3** and **4** in 40% and 50%, respectively (Fig. S32.). The yields of **3** and **4** were also confirmed by GC. Adding dodecane as an internal standard (93 mg, 0.55 mmol), which indicates the GC yields of **3** and **4** in 31% and 51%, respectively (Fig. S33.).

Fig. S32. The ^1H NMR spectrum of the mixture formed from the reaction of **1** with 3,5-di(trifluoromethyl)styrene in 48 h (Inset: expanded region of ^1H NMR spectrum of reaction mixture from 6.9 to 6.2 ppm).

Fig. S33. GC graph of the sample obtained from the reaction of **1** with 3,5-di(trifluoromethyl)styrene in 48 h.

Fig. S34. Molecular structure of **8**, showing 30% probability ellipsoids and the partial atoms numbering scheme. Selected distances (Å) and angles (deg): Pd-C1 2.146(4), Pd-C2 2.143(3), Pd-P1 2.3218(9), Pd-P2 2.2954(9), C1-Pd1-C2 38.29(14), C1-Pd-P1 145.01(10), C1-Pd-P2 118.92(10), P1-Pd-C2 106.76(10), P1-Pd-P2 96.07(3), P2-Pd-C2 156.98(10).

Fig. S35. ¹H NMR spectrum of **8** (Inset: expanded region of ¹H NMR spectrum of **8** from 8.2 to 6.2 ppm).

Fig. S36. ^{13}C NMR spectrum of **8** (Inset: expanded region of ^{13}C NMR spectrum of **8** from 138 to 130 ppm).

Fig. S37. ^{31}P NMR spectrum of **8**. The NMR data indicate the presence of two isomers of **8** with the ratio of 1:2.4, probably related to the different orientation of the styrene ligand toward the (BINAP)Pd unit that has C_2 -symmetry.

Fig. S38. ¹⁹F NMR spectrum of **8**. The NMR data indicate the presence of two isomers of **8** with the ratio of 1:2.5, probably related to the different orientation of the styrene ligand toward the (BINAP)Pd unit that has C₂-symmetry.

Fig. S39. UV-vis absorption spectrum in THF of **8** recorded at room temperature.

Fig. S40. IR spectrum of **8**.

Kinetic Studies on the Reaction of 1 with 3,5-di(trifluoromethyl)styrene. The kinetic studies monitor the increase of the characteristic ^1H NMR signal of **8** at $\delta = 7.84\text{--}7.75$ ppm formed in the reaction of **1** with excess amount of 3,5-bis(trifluoromethyl)styrene (20-40 equiv.) with 1,3,5-trimethoxybenzene as internal standard. Reactions were conducted with general procedure as follows: To a J-Young tube were added **1** (10 mg, 0.008 mmol), 1,3,5-trimethoxybenzene (2 mg, 0.01 mmol) and a certain amount of 3,5-bis(trifluoromethyl)styrene (39, 49, 59, 69, and 79 mg), respectively. Then the reaction mixtures were diluted with C_6D_6 to 500 μL . The mixtures were kept at 30 $^\circ\text{C}$ and monitored by ^1H NMR continuously. For a given reaction, the formation of **8** shows a constant half-life, *e.g.* $t_{1/2} = 24$ min for the reaction of **1** (0.016 mol/L) with 3,5-bis(trifluoromethyl)styrene (0.325 mol/L) at 30 $^\circ\text{C}$, which indicates a pseudo-first-order kinetics for the concentration of the **1** (Fig. S41.). The profile of the reaction indicates a pseudo-first-order kinetics for the concentration of the alkene (Figs. S42-S47).

Fig. S41. A representative plot for the change of the yield of the product **8** versus time for the reaction of **1** with 3,5-bis(trifluoromethyl)-styrene in C₆D₆ at 30 °C. The half-life is $t_{1/2} = 24 \text{ min}$.

Fig. S42. Plot of $\ln([P]_1/([P]_1-[P]))$ vs time for the reaction of **1** with 3,5-bis(trifluoromethyl)styrene (20 equiv.) at 30 °C.

Fig. S43. Plot of $\ln([P]_t/([P]_t - [P]))$ vs time for the reaction of **1** with 3,5-bis(trifluoromethyl)styrene (25 equiv.) at 30 °C.

Fig. S44. Plot of $\ln([P]_1/([P]_1-[P]))$ vs time for the reaction of **1** with 3,5-bis(trifluoromethyl)styrene (30 equiv.) at 30 °C.

Fig. S45. Plot of $\ln([P]_1/([P]_1-[P]))$ vs time for the reaction of **1** with 3,5-bis(trifluoromethyl)styrene (35 equiv.) at 30 °C.

Fig. S46. Plot of $\ln([P]_t/([P]_t - [P]))$ vs time for the reaction of **1** with 3,5-bis(trifluoromethyl)styrene (40 equiv.) at 30 °C.

Fig. S47. The linear dependence of the observed pseudo-first-order rate constants, k_{obs} , versus alkene concentration.

Reaction of 1 with 2,6-di(tert-butyl)-4-methylphenol: To a solution of **1** (200 mg, 0.16 mmol) in toluene (20 mL) was added 2,6-di(tert-butyl)-4-methylphenol (18 mg, 0.08 mmol) at room temperature. The color of the solution changed from green to red immediately. After stirring for 1 h, the mixture was concentrated under vacuum to leave a red residue. The resultant red solid was then washed with *n*-hexane (3×2 mL) and dried under vacuum, which leaves **9** as a red powder (135 mg, 89%). Single crystals of **9** suitable for X-ray diffraction were grown from liquid diffusion of *n*-pentane solution of 2,6-di(tert-butyl)-4-methylphenol into a concentrated toluene solution of **1** at -30 °C for days. For **9**: Anal. Calcd for C₅₉H₅₄P₂PdO: C, 74.80; H, 5.75; Found: C, 74.84; H, 5.81. Absorption spectrum (THF): λ_{max}, nm (ε, M⁻¹ cm⁻¹) = 400 (5600), 450 (9600). IR (KBr, cm⁻¹): ν = 3053 (m), 2949 (m), 2913 (m), 2878 (m), 1602 (s), 1560 (s), 1480 (m), 1435 (s), 1383 (m), 1350 (m), 1308 (m), 1225 (s), 1091 (m), 923 (m), 909 (m), 815 (m), 744 (s), 694 (s), 522 (m), 504 (s), 461 (m). ¹H NMR (400 MHz, THF-*d*₈, 298 K): δ 7.72 (t, *J* = 9.0 Hz, 2H), 7.58-7.44 (m, 6H), 7.42-6.98 (m, 16H), 6.96-6.88 (m, 2H), 6.75-6.69 (m, 1H), 6.68-6.59 (m, 3H), 6.58-6.50 (m, 2H), 6.41-6.32 (m, 2H), 2.96 (s, 1H), 2.24 (s, 1H), 1.27 (d, *J* = 30.2 Hz, 18H). ¹³C NMR (101 MHz, THF-*d*₈, 298 K): δ (ppm) 184.35, 184.32, 142.56, 142.53, 141.36, 141.33, 140.42, 140.41, 140.27, 138.25, 137.61, 137.54, 137.37, 137.33, 137.28, 137.23, 136.43, 136.41, 136.36, 135.81, 135.61, 135.54, 135.50, 135.47, 135.45, 134.95, 134.78, 134.77, 134.74, 134.70, 134.59, 134.35, 134.23, 134.17, 134.01, 133.99, 133.83, 133.45, 133.12, 130.42, 130.38, 130.36, 130.20, 130.18, 130.14, 130.04, 129.76, 129.74, 129.48, 129.16, 129.07, 128.95, 128.93, 128.71, 128.70, 128.63, 128.52, 128.43, 128.36, 128.23, 128.07, 127.99, 127.89, 127.77, 127.73, 127.66, 127.09, 127.03, 126.98, 126.79, 126.60, 126.43, 125.84, 83.86, 83.81, 83.74, 83.69, 54.47, 54.18, 35.44, 35.42, 35.37, 35.35, 29.97, 29.78. ³¹P NMR (162 MHz, THF-*d*₈, 298 K): δ (ppm) 32.03 (d, *J* = 9.9 Hz), 29.41 (d, *J* = 10.0 Hz). The *n*-hexane solutions were combined and concentrated under vacuum to leave a residue that was further purified by flash column chromatography (silica gel, *n*-hexane as elute) to give **4** as white solid (70 mg, 86%).

Fig. S48. Molecular structure of **9a**, showing one of the two crystallographically independent molecules in the unit cell with 30% probability ellipsoids and the partial atoms numbering scheme. Selected distances (Å) and angles (deg): Pd1-C7 2.111(5), Pd1-C6 2.199(6), Pd1-P1 2.3174(13), Pd1-P2 2.3202(14), O1-C3 1.247(6), C1-C2 1.363(7), C1-C6 1.445(7), C3-C2 1.500(7), C3-C4 1.471(7), C4-C5 1.332(7), C5-C6 1.437(7), C7-C6 1.421(7), C7-Pd1-C6 38.43(18), C7-Pd1-P1 156.71(14), C7-Pd1-P2 105.74(13), P1-Pd1-C6 119.31(13), P1-Pd1-P2 94.83(5), P2-Pd1-C6 143.55(13).

Fig. S49. Molecular structure of **9b**, showing another one of the two crystallographically independent molecules in the unit cell with 30% probability ellipsoids and the partial atoms numbering scheme. Selected distances (Å) and angles (deg): Pd2-C66 2.108(5), Pd2-C65 2.214(6), Pd2-P3 2.3053(14), Pd2-P4 2.3164(13), O2-C62 1.238(6), C60-C61 1.361(7), C61-C62 1.467(7), C62-C63 1.488(7), C63-C64 1.343(7), C64-C65 1.430(7), C65-C66 1.434(7), C66-Pd2-C65 38.66(17), C66-Pd2-P3 102.13(13), C66-Pd2-P4 160.67(14), P3-Pd2-C65 140.62(13), P3-Pd2-P4 95.93(5), P4-Pd2-C65 122.59(13).

Fig. S50. ¹H NMR spectrum of **9**.

Fig. S51. ¹³C NMR spectrum of **9**. (Inset: expanded region of ¹³C NMR spectrum of **9** from 142 to 126 ppm)

Fig. S52. ^{31}P NMR spectrum of **9**.

Fig. S53. UV-vis absorption spectrum in THF of **9** recorded at room temperature.

Fig. S54. IR spectrum of **9**.

Fig. S55. A probable mechanism for the reaction of **1** with 2,6-di(tert-butyl)-4-methylphenol.

Reactions of 1 with Anilines. The interaction of **1** with primary anilines, *e.g.* 2,6-di(isopropyl)aniline and *para*-substituted 2,6-dimethylanilines, in C_6D_6 led to the production of the free amine $\text{Ar}^{\text{Trip}}\text{NH}_2$ (**4**) as indicated by ^1H NMR spectrum (Figs. S56-S61). These reactions were conducted with general procedure as follows: To a J-Young tube were added **1**, 1,3,5-trimethoxybenzene and anilines. Then the reaction mixture was diluted with C_6D_6 to 500 μL . The reactions produced **4** instantly as indicated by the observation of its characteristic ^1H NMR signals in the range 3.08 to 2.99 ppm. Aiming to probe the outcome of the anilines and palladium species, the reaction of 2,6-dimethylanilines (4.3 mg, 0.0035 mmol) with **1** (43.5 mg, 0.035 mmol) was examined in detail. When the production of **4** stopped in 1 h, analyzing the ^{31}P NMR spectrum with OPPh_3 (4.5 mg, 0.016 mmol) as an internal standard indicated the formation of diamagnetic phosphine-containing species in 71% yield (Fig. S62.). The exact identity of the phosphine-palladium species is unclear. The reaction mixture is quenched with a drop of water, analyzing the ^1H NMR spectrum with 1,3,5-trimethoxybenzene (0.10 M in C_6D_6 , 100 μL) as an internal standard indicated the formation of 2,6-dimethylaniline in 93% yield (Fig. S63.).

Fig. S56. The ^1H NMR spectrum of the mixture of the reaction of **1** with one equiv. of 2,6-di(isopropyl)aniline in 1 h.

Fig. S57. The ¹H NMR spectrum of the mixture of the reaction of **1** with one equiv. of 4-(tert-butyl)-2,6-dimethylaniline in 1 h.

Fig. S58. The ^1H NMR spectrum of the mixture of the reaction of **1** with one equiv. of 2,4,6-trimethylaniline in 1 h.

Fig. S59. The ^1H NMR spectrum of the mixture of the reaction of **1** with one equiv. of 2,6-dimethylaniline in 1 h.

Fig. S60. The ^1H NMR spectrum of the mixture of the reaction of **1** with one equiv. of 4-bromo-2,6-dimethylaniline in 1 h.

Fig. S61. The ^1H NMR spectrum of the mixture of the reaction of **1** with one equiv. of 4-amino-3,5-dimethylbenzonitrile in 1 h.

Fig. S62. The ^{31}P NMR spectrum of the mixture of the reaction of **1** with one equiv. of 2,6-dimethylaniline. The spectrum indicates the total yield of diamagnetic phosphine-containing species reaches 71%.

Fig. S63. The ¹H NMR spectrum of the mixture of the reaction of **1** with one equiv. of 2,6-dimethylaniline after quenched with water. The spectrum clearly shows the regeneration of 2,6-dimethylaniline.

Isotope Kinetic Effect of the Reactions 1 with 2,6-dimethylaniline and *N,N'*-dideuterium-2,6-dimethylaniline. To a J-Young tube were added **1** (35 mg, 0.028 mmol), 1,3,5-trimethoxybenzene (0.10 M in C₆D₆, 60 μL), 2,6-dimethylaniline (3.5 mg, 0.028 mmol) or *N,N'*-dideuterium-2,6-dimethylaniline (3.5 mg, 0.028 mmol). Then the reaction mixture was diluted with C₆D₆ to 500 μL. Monitoring the increase of the ¹H NMR signal of **4** at δ = 3.08-2.99 ppm versus time gave the kinetic profile shown in Fig. 5.

Substituent Effects of the Reactions of 1 with *para*-substituted 2,6-dimethylanilines. The study was conducted with general procedure as follows: To a J-Young tube were added **1** (35 mg, 0.028 mmol), 1,3,5-trimethoxybenzene (0.10 M in C₆D₆, 60 μL), and a *para*-substituted 2,6-dimethylaniline (0.10 M in C₆D₆, 280 μL). Then the reaction mixture was diluted with C₆D₆ to 500 μL. The yields of **4** versus time was followed by the increase of the ¹H NMR signal at δ = 3.08-2.99 ppm. The initial rates in the first 10 minutes were used (Fig. S64). The Hammett plot with *para*-substituted 2,6-dimethylanilines is shown in Fig. 5.

Fig. S64. The plot of the yields of **4** vs time in the reactions of **1** with different anilines.

Reactions of 1 with *n*-butyl amine and *n*-octyl amine. These reactions were conducted with general procedure as follows: To a J-Young tube were added **1** (50 mg, 0.04 mmol), 1,3,5-trimethoxybenzene (2.8 mg, 0.02 mmol) and *n*-butyl amine (3 mg, 0.04 mmol). The production of **4** stopped in 1 h, and the ¹H NMR yield of **4** reached 94%. The other J-Young tube were added **1** (50 mg, 0.04 mmol), 1,3,5-trimethoxybenzene (3.2 mg, 0.02 mmol) and *n*-octyl amine (5.3 mg, 0.04 mmol). The production of **4** stopped in 1 h, and the ¹H NMR yield of **4** is found to be 91%.

^1H NMR, C_6D_6 , 400 MHz

Fig. S65. The ^1H NMR spectrum of the mixture of the reaction of **1** with one equiv. of *n*-butyl amine in 1 h.

^1H NMR, C_6D_6 , 400 MHz

Fig. S66. The ^1H NMR spectrum of the mixture of the reaction of **1** with one equiv. of *n*-octyl amine in 1 h.

Preparation of [(BINAP)Pd(OAc)₂] (6). To a solution of Pd(OAc)₂ (200 mg, 0.89 mmol) in THF (20 mL) was added BINAP (552 mg, 0.89 mmol) at room temperature. The color of the solution changed from red to yellow. After stirring for 2 h, the yellow precipitate was collected by filtration. The resultant yellow solid was then washed with THF (3×2 mL) and dried under vacuum, which leaves [(BINAP)Pd(OAc)₂] (6) as a yellow powder (653 mg, 87%). Single crystals of **6** • CH₂Cl₂ suitable for X-ray diffraction were grown by diffusion of pentane into a concentrated CH₂Cl₂ solution of **6** at room temperature for days. For **6**: Anal. Calcd for C₄₈H₃₈P₂PdO₄•CH₂Cl₂: C, 63.14; H, 4.33; Found: C, 63.43; H, 4.52. Absorption spectrum (THF): λ_{max}, nm (ε, M⁻¹ cm⁻¹) = 320 (5400), 350 (3200). IR (KBr, cm⁻¹): ν = 3051 (w), 1607 (s), 1584 (s), 1500 (s), 1481 (w), 1435 (m), 1366 (s), 1315 (s), 1222 (w), 1118 (w), 1159 (w), 1096 (w), 996 (w), 918 (w), 871 (w), 745 (s), 695 (s), 673 (s), 609 (w), 525 (m), 503 (s), 477 (w), 438 (w). ¹H NMR (400 MHz, CDCl₃, 293 K): δ 7.88 (s, 4H), 7.77 (s, 4H), 7.59-7.52 (m, 4H), 7.49 (s, 8H), 7.37-7.29 (m, 2H), 7.05-6.97 (m, 2H), 6.78-6.72 (m, 2H), 6.68 (s, 4H), 6.52 (d, *J* = 8.7 Hz, 2H), 1.33 (s, 6H). ¹³C NMR (101 MHz, CDCl₃, 293 K): δ (ppm) 176.87, 138.94, 135.40, 135.17, 134.05, 132.87, 130.93, 129.95, 129.09, 128.16, 128.11, 128.05, 127.65, 127.45, 126.75, 126.49, 126.20, 122.80, 122.21, 23.02. ³¹P NMR (162 MHz, CDCl₃, 293 K): δ (ppm) 25.42.

Fig. S67. Molecular structure of **6**, showing 30% probability ellipsoids and the partial atoms numbering scheme. Selected distances (Å) and angles (deg): Pd1-P1 2.2415(8), Pd1-P2 2.2358(8), Pd1-O1 2.096(2), Pd1-O3 2.085(2), O1-Pd1-O3 89.68(9), O1-Pd-P1 90.47(7), O1-Pd-P2 168.73(6), P1-Pd-P2 91.78(3).

Fig. S68. ^1H NMR spectrum of **6**.

Fig. S69. ¹³C NMR spectrum of **6**.

Fig. S70. ^{31}P NMR spectrum of **6**.

Fig. S71. UV-vis absorption spectrum in DCM of **6** recorded at room temperature.

Fig. S72. IR spectrum of **6**.

Details for single-crystal X-ray diffraction study.

Diffraction-quality crystals were obtained from recrystallizations in Et₂O at -30 °C (**1**), *n*-hexane at room temperature (**2**), DCM/*n*-pentane at room temperature (**6**•CH₂Cl₂), toluene at -30 °C (**7**), toluene/*n*-hexane at room temperature (**8**•0.5 *n*-hexane) and toluene/*n*-pentane at -30 °C (**9**). Crystals were coated with Paratone-N oil and mounted on a Bruker APEX-II CCD-based diffractometer or a Bruker D8 Venture diffractometer equipped with an Oxford low-temperature apparatus. Cell parameters were retrieved with SMART software and refined using SAINT software on all reflections. Data integration was performed with SAINT, which corrects for Lorentz polarization and decay. Absorption corrections were applied using SADABS(58). Space groups were assigned unambiguously by analysis of symmetry and systematic absences determined by XPREP. All structures were solved and refined using SHELXTL (59). Metal and first coordination sphere atoms were located from direct-methods E-maps. Non-hydrogen atoms were found in alternating difference Fourier synthesis and least-squares refinement cycles and during final cycles were refined anisotropically. Table S2 summarizes the crystal data and summary of data collection and refinement for the complexes. CCDC 2059309-2059313 and 2070924 contain the supplementary crystallographic data for complexes **1**, **2**, **6**•CH₂Cl₂, **7**, **8**•0.5 *n*-hexane and **9**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S2. Crystal data and summary of data collection and refinement for **1**, **2**, **6•CH₂Cl₂**, **7**, **8•0.5 *n*-hexane**, and **9**.

	1 (170 K)	2 (170 K)	6•CH₂Cl₂ (170 K)	7 (170 K)	8•0.5 <i>n</i>-hexane (170 K)	9 (193 K)
formula	C ₈₀ H ₈₂ NP ₂ Pd	C ₇₂ H ₁₀₀ N ₂	C ₄₉ H ₄₀ Cl ₂ O ₄ P ₂ Pd	C ₆₂ H ₅₀ N ₂ P ₂ Pd	C ₅₇ H ₄₅ F ₆ P ₂ Pd	C ₅₉ H ₅₄ OP ₂ Pd
crystal size (mm)	0.08 x 0.06 x 0.05	0.08 x 0.06 x 0.06	0.08 x 0.06 x 0.05	0.08 x 0.05 x 0.03	0.1 x 0.09 x 0.01	0.17 x 0.14 x 0.11
fw	1225.81	993.53	932.05	991.38	1012.27	947.36
crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Tetragonal
space group	P -1	P 21/n	P 21/n	P ccn	P 21/c	I 41
<i>a</i> , Å	16.0516(3)	11.9371(2)	11.9235(6)	9.8868(2)	14.7215(3)	35.6442(11)
<i>b</i> , Å	20.4836(3)	18.2398(3)	22.0145(11)	20.7049(5)	12.0486(2)	35.6442(11)
<i>c</i> , Å	23.0650(4)	29.9062(5)	16.1565(8)	23.7699(6)	26.9307(5)	17.0827(6)
<i>α</i> , deg	110.5920(10)	90	90	90	90	90
<i>β</i> , deg	93.5900(10)	95.9090(10)	94.297(2)	90	102.2910(10)	90
<i>γ</i> , deg	96.2250(10)	90	90	90	90	90
<i>V</i> , Å ³	7015.2(2)	6476.89(19)	4229.0(4)	4865.8(2)	4667.30(15)	21703.7(15)
<i>Z</i>	4	4	4	4	4	16
<i>D</i> _{calcd} , Mg/m ³	1.161	1.019	1.464	1.353	1.441	1.160
radiation (λ), Å	Ga Kα (1.34139)	Ga Kα (1.34139)	Ga Kα (1.34139)	Ga Kα (1.34139)	Ga Kα (1.34139)	Mo Kα (0.71073)
2θ range, deg	2.9 to 54.9	3.4 to 54.9	3.0 to 55.1	4.6 to 54.9	2.9 to 55.0	4.6 to 51.0
μ, mm ⁻¹	1.903	0.274	3.835	2.666	2.898	0.437
<i>F</i> (000)	2580	2184	1904	2048	2068	7872
no. of obsd rflns	85654	69949	31691	30005	50206	52901
no. of params refnd	1567	696	525	305	596	1156
goodness of fit	0.996	1.031	1.100	1.057	1.024	0.997
R1	0.0415	0.0768	0.0387	0.0437	0.0441	0.0372
wR2	0.0923	0.1854	0.1055	0.1207	0.0987	0.0779
CCDC	2059309	2059310	2070924	2059311	2059312	2059313

Details for EPR spectroscopy.

9 GHz (X-band) continuous wave (CW) EPR spectrum was collected on a Bruker EMX plus 6/1 spectrometer equipped with an Oxford Instrument ESR900 liquid He cryostat using an Oxford ITC 503 temperature controller. The spectrum was collected with the following experimental parameters: microwave frequency, 9.6 GHz; microwave power, 0.3 mW; modulation amplitude, 10 G; time constant, 20.48 ms; 4 scans; temperature, 70 K. EPR spectrum in toluene solution was obtained with the following experimental parameters: microwave frequency, 9.4 GHz; microwave power, 0.15 mW; modulation amplitude, 1 G; 1 scan; temperature 295 K. 34 GHz (Q-band) electron spin echo(ESE) detected EPR spectrum was collected using an EN5107D2 resonator. The spectrum was acquired using a pulse sequence, $\pi/2$ - τ - π -echo, with a pulse length $t_{\pi/2} = 32$ ns, $t_{\pi} = 64$ ns and $\tau = 200$ ns; temperature, 20 K. 94 GHz (W-band) CW EPR spectrum was obtained on a Bruker Eleksys E680 spectrometer with a cylindrical high Q-resonator (EN680-1021H) and cryogenic temperatures were achieved with an Oxford CF-935 cryostat and Oxford MercuryiTC temperature controller. The spectrum was obtained with the following experimental parameters: microwave frequency, 93.9 GHz; microwave power, 0.05 mW; modulation amplitude, 10 G; time constant, 81.92 ms; temperature, 82 K. The simulations of the EPR spectra were performed by EasySpin (60).

Fig. S73. Solution EPR spectrum of **1**(black line) and simulations (red line)

Details for X-ray absorption spectroscopy.

Data Collection. All data were measured at the Stanford Synchrotron Radiation Lightsource (SSRL) under ring conditions of 3.0 GeV and 500 mA. Samples were prepared in an inert-atmosphere glovebox where they were ground to a fine powder with BN to a final concentration of 5 weight % Pd. For Pd K-edge measurements, the powder was pressed into 1 mm aluminum spacers and sealed with 37 μm Kapton tape. For Pd L-edge measurements, the powder was pressed into 1 mm aluminum spacers with a 38 μm low-S Mylar tape backing and sealed with polyfilm.

Pd K-edge measurements were carried out at beamline 9-3 equipped with a 16-pole, 2-Tesla wiggler source. A double Si(220) crystal was used as a monochromator. Samples were maintained at 10 K in a liquid He cryostat. Spectra were measured in fluorescence mode using a passivated implanted planar silicon (PIPS) detector placed at a 90° angle to the sample. Soller slits fitted with a Ni filter were included to attenuate inelastic scattering. A Pd foil and a third ionization chamber upstream of the sample were used for internal energy calibration. Two scans were measured and averaged for each compound.

Pd L_{2,3}-edge measurements were collected on beamline 4-3 equipped with a 20-pole, 2-Tesla wiggler source. Spectra were collected on samples in a He atmosphere at room temperature using fluorescence mode with a Lytle detector. Intensity was normalized with respect to the incident beam using a He-filled ion chamber upstream of the sample. Two scans were measured and averaged for each compound.

Data Processing. Raw Pd K- and L-edge measurements were averaged and normalized using SIXPACK (61) and processed using Igor 6.37. Energies of the palladium K-edges were calibrated by setting the inflection point of a Pd foil scan to 24350.3 eV. Background was removed by applying a linear normalization to the pre-edge region below 24300 eV. The edge-jump was normalized to unit intensity by applying a quadratic normalization to the post-edge region above 24410 eV. Rising-edge energies were determined by the first maximum in the first derivative after Savitzsky-Golay smoothing was applied in Igor.

Pd L-edge energies were calibrated by setting the inflection point of the L₃-edge of a Pd foil scan to 3173.3 eV. Background was removed by applying a linear fit to the pre-edge region below

3158 eV and subtracting it from the entire spectrum. Normalization was achieved using the L₂-edge, where the post-edge region was fit to a quadratic in the region between 3358 eV and 3608 eV and normalized to unit intensity. The edge jumps were removed in PyMCA (62) with a statistics-sensitive non-linear iterative peak-clipping (SNIP) algorithm (63), using a background width of 21. L₃ and L₂ peak areas were obtained separately using the multiple peak-fitting feature in Igor (Figs. S74 and S75). To minimize error, a mixture of Voigt and Gaussian peaks was used. Only the first peak corresponding to the mainline was used to calculate the area.

Fig. S74. Overlay of experimental Pd K-edge XAS spectra of $\text{Pd}^0(\text{NHC})_2$ (5, blue), $(\text{BINAP})\text{Pd}^{\text{I}}(\text{NHAr}^{\text{Trip}})$ (1, red), and $(\text{BINAP})\text{Pd}^{\text{II}}(\text{OAc})_2$ (6, black).

Fig. S75. Experimental $L_{2,3}$ -edges of (BINAP)Pd^I(NHAr^{Trip}) (**1**) and (BINAP)Pd^{II}(OAc)₂ (**6**). Spectra were normalized to unit intensity in the L_2 post-edge region and the edge jumps were removed.

Fig. S76. Peak-fit of the experimental L₃-edge (left) and L₂-edge (right) of (BINAP)Pd^I(NHAr^{Trip}) (1). The overall fit is represented as a black dashed line and the individual peaks are shown in grey.

Fig. S77. Peak-fit of the experimental L₃-edge (left) and L₂-edge (right) of (BINAP)Pd^{II}(OAc)₂ (**6**). The overall fit is represented as a black dashed line and the individual peaks are shown in grey.

Computational Details.

DFT and TDDFT calculations were performed using ORCA version 4.2 (64). The molecular structures of **1** and **8** obtained from single-crystal X-ray diffraction study was used directly for SCF calculations without further structure optimization. Single-point energies were calculated using crystallographic coordinates and the B3LYP functional (65-68). The RIJCOSX (69) approximation with auxiliary basis sets built using the ORCA AUTOAUX method (70) was employed to accelerate the calculations. The SARC-ZORA (71) basis set was used for palladium and the ZORA-def2-TZVP(-f) basis set (72) was used for all other atoms. Special integration accuracy (ORCA Grid7) was used for palladium and phosphorus, while ORCA Grid4 was used for all other atoms. The zeroth-order regular approximation (ZORA) (73) for relativistic effects and the atom-pairwise dispersion correction with Becke-Johnson damping (44, 74) were included. Solvation was modeled with the conductor-like polarizable continuum model (CPCM) (75) in an infinite dielectric. The UV/vis absorption spectrum of **1** was calculated using the aforementioned single-point DFT calculation as a starting point. 50 roots were calculated for the UV/vis absorption spectrum. Pd L-edge XAS spectra were calculated using TDDFT with 50 root excitations and restricting donor orbitals to the Pd 2p orbitals and acceptor orbitals to the first 20 empty orbitals. Spectra were plotted using a linewidth broadening of 1 eV. Calculated energies were shifted by the average of the requisite shifts for the L₃ pre-edge and TDDFT calculated pre-edge of **1** and **6**.

For bonding analysis, the geometries were optimized without symmetry constraint within the DFT (density functional theory) framework using the B3LYP functional (76, 77) in combination with the Grimme Dispersion corrections with the Becke-Johnson damping function D3(BJ) (74) and the Ahlrichs def2-SVP basis function (78). Geometry optimization for the mononuclear Pd(I) Amido Complex **1** was conducted at B3LYP/def2-SVP level, which agree with the experimental structure very well (see Fig. S82.). These calculations were performed using Gaussian 16 A03 software (79).

Energy decomposition analysis (EDA) was performed at the B3LYP/TZ2P(50) level using the ADF2019.01 software (80). In the EDA scheme, the interaction energy (ΔE_{int}) has been decomposed into four terms as,

$$\Delta E_{int} = \Delta E_{Pauli} + \Delta E_{elstat} + \Delta E_{orb} + \Delta E_{disp} \quad (1)$$

where, ΔE_{elstat} corresponds to the classical electrostatic energy between those fragments and it is generally attractive in nature. The next attractive term is orbital interaction energy, ΔE_{orb} , which arises from the charge transfer and mixing of the occupied and unoccupied orbitals on the fragments and polarization effects. The ΔE_{disp} represents the dispersion energy correction towards the total attraction energy. The only repulsive contribution is the Pauli interaction energy (ΔE_{Pauli}) and it is originated from the repulsion between the occupied orbitals of the interacting fragments.

The EDA-NOCV calculation combines the energy and charge decomposition schemes and divide the deformation density, $\Delta\rho(r)$, associated with the bond formation into different components (σ, π, δ) of a chemical bond. From the mathematical point of view, each NOCV, ψ_i is defined as an eigenvector of the deformation density matrix in the basis of fragment orbitals.

$$\Delta P_{\psi_i} = v_i \psi_i \quad (2)$$

In EDA-NOCV, ΔE_{orb} is given by the following equation,

$$\Delta E_{orb} = \sum_k \Delta E_k^{orb} = \sum_{k=1}^{N/2} v_k [-F_{-k}^{TS} + F_k^{TS}] \quad (3)$$

where, $-F_{-k}^{TS}$ and F_k^{TS} are diagonal Kohn-Sham matrix elements corresponding to NOCVs with the eigenvalues $-v_k$ and v_k , respectively. The ΔE_k^{orb} terms are assigned to a particular type of bond by visual inspection of the shape of the deformation density, $\Delta\rho_k$. The EDA-NOCV scheme thus provides both qualitative ($\Delta\rho_{orb}$) and quantitative (ΔE_{orb}) information about the strength of orbital interactions in chemical bonds. More details on the EDA-NOCV method and its application to the analysis of the chemical bond can be found in recent reviews articles (81-83). Table S3 compiles all the calculated interaction energies of each term. Figs. S83-S86 show the main components of orbital contribution.

Fig. S78. Experimental (black) and TDDFT-calculated (red, B3LYP, SARC-ZORA on Pd, ZORA-def2-TZVP(-f) on all other atoms) UV/vis absorption spectra of **1**. Individual transitions are indicated as grey sticks. The major (>5% weight) excitations giving rise to the ca. 800 nm charge transfer band are given, with relevant orbitals printed to the right at an isovalue of 0.03 au.

Fig. S79. Experimental (red) and TDDFT calculated (black) Pd L₃-edge XAS spectra of (BINAP)Pd^{II}(OAc)₂ (**6**). The B3LYP functional and SARC-ZORA basis set was used for Pd, with ZORA-def2-TZVP(-f) used for all other atoms. Contributions of individual orbitals were obtained from Löwdin population analysis of the QROs. Orbitals are plotted at an isovalue of 0.03 au with hydrogen atoms removed for clarity.

Fig. S80. Frontier MO diagram of [(BINAP)Pd^I(NHAr^{Trip})] (**1**) and [(BINAP)Pd^{II}(OAc)₂] (**6**). Energies were obtained from the QROs (calculated using the B3LYP level of theory with the SARC-ZORA basis set on Pd and ZORA-def2-TZVP(-f) on all other atoms). Acceptor orbitals in the calculated L₃-edge mainline are labeled in red. Orbitals are plotted at an isovalue of 0.03 au with hydrogen atoms removed for clarity.

Fig. S81. Correlation between the total area of the $L_{2,3}$ -edge mainlines of [(BINAP)Pd^I(NHAr^{TRIP})] (**1**) and [(BINAP)Pd^{II}(OAc)₂] (**6**) and the calculated Pd d character per hole of all acceptor orbitals. Error in the slope is estimated at 3.21 and error in the intercept is estimated at 8.07.

Pd2-P3	= 2.383 [2.321]
Pd2-P4	= 2.374 [2.284]
Pd2-N2	= 2.083 [2.063]
N2-C125	= 1.368 [1.371]
∠Pd2-N2-C125	= 143.0[140.0]
∠P4-Pd2-N2	= 143.9[149.5]
∠P3-Pd2-P4	= 93.4 [92.1]
∠P3-Pd2-N2	= 119.8[114.4]

Fig. S82. Optimized structure of the Mononuclear Pd(I) Amido Complex **1** at the B3LYP/def2-SVP or level of theory. Key bond distances(Å), and bond angles(°) are given in angstroms and degrees, respectively. The corresponding experimental values are given in the bracket. Color code: Pd, light green; P, orange; N, blue; C, gray. Hydrogen atoms have been omitted for clarity.

Table S3. EDA-NOCV results of [(BINAP)Pd(NHAr^{Trip})] (**1**) at the B3LYP+(D3BJ)/TZ2P//B3LYP/def2-SVP level of theory. Fragments are given in singlet (S) or doublet (D) electronic states. Energy values are given in kcal/mol.

Fragments	[(BINAP)Pd ⁰](S) + NHAr ^{Trip} (D)	[(BINAP)Pd ^I] ⁺ (D) +[NHAr ^{Trip}] ⁻ (S)	[(BINAP)Pd ^I] ⁻ (D) +[NHAr ^{Trip}] ⁺ (S)
ΔE_{int}	-72.4	-139.0	-221.8
ΔE_{Pauli}	123.1	129.5	126.0
$\Delta E_{\text{disp}}^{[a]}$	-31.3(16.0%)	-31.3(11.7%)	-31.3(9.0%)
$\Delta E_{\text{elstat}}^{[a]}$	-92.3(47.2%)	-163.5(60.9%)	-125.3(36.0%)
$\Delta E_{\text{orb}}^{[a]}$	-72.0(36.8%)	-73.7(27.4%)	-191.3(55.0%)
$\Delta E_{\text{orb1}}^{[b]}$	-43.2(59.9%)	-23.8(32.3%)	
$\Delta E_{\text{orb2}}^{[b]}$	-16.9(23.5%)	-23.2(31.5%)	
ΔE_{rest}	-11.9(16.6%)	-26.7(36.2%)	
ΔE_{prep}	21.5	17.7	
$\Delta E = -D_e$	-50.9	-121.3	

^aThe values in parentheses give the percentage contribution to the total attractive interactions $\Delta E_{\text{elstat}} + \Delta E_{\text{orb}} + \Delta E_{\text{disp}}$.

^bThe values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb} .

$$\Delta E_{\text{orb}(1)} = \Delta E_{\text{orb}(1\beta)} = -43.2 \text{ kcal/mol}$$

$$v = \pm 0.832$$

$$\Delta E_{\text{orb}(1\alpha)} = -8.8 \text{ kcal/mol}$$

$$v = \pm 0.227$$

$$\Delta E_{\text{orb}(2\beta)} = -8.1 \text{ kcal/mol}$$

$$v = \pm 0.204$$

$$\Delta E_{\text{orb}(2)} = \Delta E_{\text{orb}(1\alpha)} + \Delta E_{\text{orb}(2\beta)} = -16.9 \text{ kcal/mol}$$

$$v = \pm 0.431$$

Fig. S83. Plot of deformation densities $\Delta\rho$ of the pairwise orbital interactions between the $[(\text{BINAP})\text{Pd}^0](\text{S}) + \text{NHA}^{\text{Trip}}(\text{D})$ two fragments in their neutral states in $[(\text{BINAP})\text{Pd}(\text{NHA}^{\text{Trip}})]$ (**1**) together with the associated interaction energies ΔE_{orb} (in kcal/mol). The eigenvalues v are a measure for the relative amount of charge transfer. The direction of the charge flow is from red to blue.

Fig. S84. Shape of the most important interacting MOs of the $[(\text{BINAP})\text{Pd}^0](\text{S}) + \text{NHA}^{\text{Trip}}$ (D) two fragments in their neutral states in $[(\text{BINAP})\text{Pd}(\text{NHA}^{\text{Trip}})]$ (**1**), plot of deformation densities $\Delta\rho$ of the pairwise orbital interactions and the associated interaction energies (ΔE_{orb}) between fragments. The numbers in bracket are SFO contribution. The direction of the charge flow is red to blue.

Fig. S85. Plot of deformation densities $\Delta\rho$ of the pairwise orbital interactions between the $[(\text{BINAP})\text{Pd}^{\text{I}}]^+(\text{D}) + [\text{NHA}^{\text{Trip}}]^-(\text{S})$ two fragments in $[(\text{BINAP})\text{Pd}(\text{NHA}^{\text{Trip}})]$ (**1**) together with the associated interaction energies ΔE_{orb} (in kcal/mol). The eigenvalues v are a measure for the relative amount of charge transfer. The direction of the charge flow is from red to blue.

Fig. S86. Shape of the most important interacting MOs of the $[(\text{BINAP})\text{Pd}]^+(\text{D}) + [\text{NHA}^{\text{Trip}}]-(\text{S})$ two fragments in $[(\text{BINAP})\text{Pd}(\text{NHA}^{\text{Trip}})]$ (**1**), plot of deformation densities $\Delta\rho$ of the pairwise orbital interactions and the associated interaction energies (ΔE_{orb}) between fragments. The numbers in bracket are SFO contribution. The direction of the charge flow is red to blue.

Fig. S87. Schematic representation of electronic resonance about Pd and N in the $[(\text{BINAP})\text{Pd}(\text{NHAr}^{\text{TRIP}})]$ (a) ; Plot of the spin density of the $[(\text{BINAP})\text{Pd}(\text{NHAr}^{\text{TRIP}})]$ at the B3LYP/def2-SVP level (b).

Data S1. (separate file)

Type or paste caption here.

Cartesian coordinates (Å) and energies(in hartree) at the B3LYP/def2-SVP level

Mononuclear Pd(I) Amido Complex 1

Energy= -3960.9591951

Pd	0.069792	0.207118	-0.119940
P	-1.001160	-1.337644	1.344525
P	-1.821271	0.386506	-1.543461
N	2.135137	0.463824	-0.023177
H	2.525738	-0.419250	-0.355818
C	-2.806938	-0.973459	1.569408
C	-3.761502	-1.150721	0.556675
C	-3.456057	-1.843998	-0.745562
C	-2.720189	-1.236130	-1.774576
C	-3.131448	1.619684	-1.149131
C	-2.813783	2.650928	-0.250642
H	-1.821806	2.687875	0.206747
C	-3.760470	3.631969	0.060852
H	-3.500792	4.424324	0.766488
C	-5.028862	3.596885	-0.524337
H	-5.768640	4.363040	-0.278131
C	-5.352293	2.574237	-1.422019
H	-6.345706	2.535999	-1.875804
C	-4.411265	1.589372	-1.730086
H	-4.679030	0.786835	-2.420885
C	-1.292513	0.839623	-3.266501
C	-0.059243	0.335263	-3.719746
H	0.545706	-0.283837	-3.051463
C	0.407807	0.629273	-5.002425
H	1.366774	0.223845	-5.334583
C	-0.338053	1.457875	-5.846974
H	0.031952	1.700864	-6.846350
C	-1.551661	1.985565	-5.398939
H	-2.135161	2.645189	-6.046632
C	-2.029056	1.676739	-4.120700
H	-2.977810	2.101953	-3.791239
C	-2.531126	-1.936010	-3.002859
H	-1.966913	-1.462884	-3.805534
C	-3.047108	-3.192537	-3.208083
H	-2.888846	-3.700526	-4.163284

C	-3.792384	-3.845067	-2.193939
C	-4.005347	-3.163867	-0.949893
C	-4.763806	-3.843074	0.050309
H	-4.941967	-3.353457	1.007427
C	-5.277238	-5.104634	-0.167865
H	-5.855664	-5.596595	0.618427
C	-5.062037	-5.768601	-1.400488
H	-5.474376	-6.767743	-1.562064
C	-4.331916	-5.147346	-2.389736
H	-4.155161	-5.645926	-3.346697
C	-5.113902	-0.686601	0.767639
C	-5.463287	-0.029366	1.994129
C	-4.457515	0.161341	2.976173
H	-4.712910	0.673896	3.907523
C	-3.178467	-0.291164	2.767957
H	-2.428724	-0.125226	3.540928
C	-6.797195	0.418373	2.203403
H	-7.037251	0.916387	3.146785
C	-7.768101	0.229044	1.244114
H	-8.791025	0.572822	1.416841
C	-7.432249	-0.412568	0.027531
H	-8.199484	-0.559711	-0.737039
C	-6.145126	-0.851703	-0.204873
H	-5.912608	-1.337826	-1.151631
C	-0.341974	-1.429082	3.080420
C	-0.866116	-2.284520	4.067977
H	-1.716436	-2.930836	3.844377
C	-0.314918	-2.311250	5.349772
H	-0.735514	-2.978840	6.106394
C	0.771884	-1.486500	5.666353
H	1.201270	-1.507942	6.671425
C	1.304789	-0.641123	4.692041
H	2.157100	0.001906	4.925287
C	0.751920	-0.614847	3.405845
H	1.175660	0.039073	2.640510
C	-0.848112	-3.097617	0.793227
C	0.191826	-3.413024	-0.097211
H	0.819713	-2.610885	-0.492667
C	0.427179	-4.737364	-0.479295
H	1.243191	-4.962855	-1.170365
C	-0.377595	-5.763843	0.020624
H	-0.196252	-6.799633	-0.277736
C	-1.421800	-5.459890	0.972000
H	-2.064619	-6.255649	1.284504

C	-1.655316	-4.137724	1.283765
H	-2.484549	-3.918383	1.958365
C	3.124415	1.122334	0.654670
C	4.406762	0.487898	0.859785
C	4.722092	-0.846039	0.230629
C	4.644323	-2.051523	0.974363
C	5.013647	-3.259192	0.361819
H	4.960278	-4.185552	0.939613
C	5.453298	-3.326612	-0.962937
C	5.520879	-2.128795	-1.683363
H	5.870517	-2.149749	-2.719129
C	5.170072	-0.895618	-1.117959
C	5.330919	0.368149	-1.963046
H	4.910597	1.205397	-1.389409
C	6.817294	0.692599	-2.199563
H	7.356858	0.801602	-1.245924
H	6.926242	1.636072	-2.759958
H	7.317798	-0.101386	-2.778710
C	4.558449	0.295618	-3.290723
H	4.942749	-0.499505	-3.950872
H	4.646156	1.247590	-3.839362
H	3.487846	0.106482	-3.116091
C	5.842681	-4.660342	-1.589434
H	5.718836	-5.427335	-0.804896
C	4.911312	-5.043344	-2.752756
H	3.858288	-5.065686	-2.429683
H	5.167055	-6.039460	-3.150657
H	4.989159	-4.323036	-3.583803
C	7.317504	-4.688272	-2.026134
H	7.514633	-3.956425	-2.826726
H	7.593631	-5.683701	-2.411860
H	7.987433	-4.450304	-1.185147
C	4.208966	-2.068569	2.438832
H	3.683758	-1.120741	2.630805
C	3.234094	-3.210947	2.766756
H	2.374585	-3.222666	2.079827
H	2.843854	-3.096814	3.789943
H	3.721336	-4.198234	2.712865
C	5.426593	-2.115009	3.381667
H	6.011012	-3.037481	3.226508
H	5.103815	-2.094854	4.436106
H	6.099464	-1.260358	3.218124
C	5.407502	1.134030	1.588488
H	6.368537	0.629759	1.722167

C	5.212369	2.411330	2.121075
H	6.002454	2.906429	2.690199
C	4.005344	3.063533	1.863588
H	3.869095	4.091287	2.210189
C	2.965596	2.470492	1.131986
C	1.802793	3.369730	0.793712
C	0.879410	3.781471	1.788116
C	-0.047615	4.794179	1.492022
H	-0.743945	5.119349	2.271195
C	-0.101783	5.422661	0.245327
C	0.792915	4.98000	-0.735512
H	0.773286	5.448914	-1.720276
C	1.739548	3.976590	-0.491452
C	2.745078	3.631341	-1.589952
H	3.110879	2.616701	-1.385811
C	2.132122	3.605132	-2.998125
H	1.238477	2.964997	-3.038769
H	2.863824	3.209193	-3.720820
H	1.848160	4.610254	-3.351014
C	3.955441	4.584088	-1.543751
H	3.644812	5.623832	-1.742080
H	4.702401	4.304901	-2.306119
H	4.450564	4.560681	-0.561652
C	-1.052817	6.592134	0.011157
H	-1.873595	6.484939	0.743428
C	-0.351964	7.931290	0.312538
H	0.054471	7.949217	1.335713
H	-1.051429	8.777612	0.206275
H	0.488505	8.097170	-0.381693
C	-1.685411	6.610511	-1.387813
H	-0.935129	6.804169	-2.171607
H	-2.439549	7.411406	-1.458791
H	-2.178515	5.654810	-1.621986
C	0.869665	3.182254	3.194385
H	1.558842	2.324911	3.187400
C	1.389197	4.175195	4.250655
H	1.402772	3.709659	5.250521
H	0.747164	5.069916	4.308217
H	2.411200	4.512579	4.022486
C	-0.520158	2.655479	3.590198
H	-1.251032	3.472895	3.703468
H	-0.472198	2.121315	4.552893
H	-0.911585	1.958212	2.834362