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Eight-membered Palladacycles Derived from the Insertion of Olefines into the Pd–C Bond of Ortho-palladated Pharmaceuticals Phenethylamine and Phentermine. Synthesis of Stable Heck-type Intermediates Containing Accessible *β*-Hydrogens and its Use in the Synthesis of 2-Styryl-phenethylamines, Tetrahydroisoquinolines and Eight-membered Cyclic Amidines[†]

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Keywords

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[†] Dedicated to Prof. Aurelia Arcas and Maria-Teresa Chicote on occasion of their 60 birthdays.

Summary

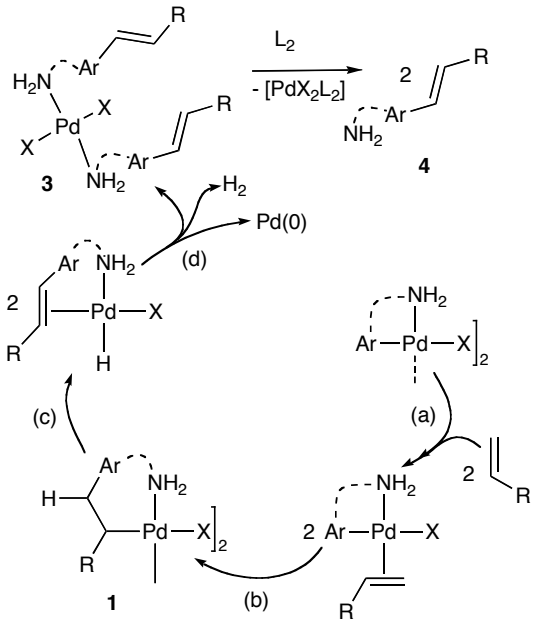
The ortho-metalated complexes derived from phenethylamine and phentermine [Pd(*C,N*-$C_6H_4CH_2CR_2NH_2$-2)(μ-X)]$_2$ (R = H, X = Br (**A**); R = Me, X = Cl (**B**)) react with olefins giving (1) the product of its insertion into the Pd–C bond, [Pd{*C,N*-CH(R')$CH_2C_6H_4CH_2CR_2NH_2$-2}(μ-X)]$_2$ (olefin = CH_2=CHR'; R = H, X = Cl, R' = C(O)Me (**1a**), CO_2Et (**1c**); R = Me, X = Cl, R' = C(O)Me (**1b**), CO_2Et (**1d**)), [Pd{*C,N*-CH(C_5H_8)$CHC_6H_4(CH_2CMe_2NH_2)$-2}(μ-Cl)]$_2$ (olefin = norbornene, C_5H_8; **1e**) or (2) the decomposition products of **1**, i.e., Pd(0) and the complexes containing the arylated olefin, *trans*-[$PdX_2(NH_2CR_2CH_2C_6H_4CH$=CHPh-2)$_2$] (olefin = styrene; R = H, X = Cl (**3f**); R = Me, X = Br (**3g**)). While complexes **1c** and **1d** can be isolated but decompose in solution to afford Pd(0) and the corresponding complexes **3** (R = H, X = Cl (**3c**); R = Me, X = Br (**3d**)), the others are surprisingly stable. Neutral ligands L cleave the bridge of complexes **1** to afford [Pd(C^N)X(L)] (**2**) (L = 4-methyl-pyridine (pic), NH_3, $NHEt_2$, PPh_3, ^{t}BuNC, XyNC). Complexes **3** react with 1,10-phenanthroline (phen) to give [PdX_2(phen)] and the ortho-vinylated arylalkylamine RCH=$CHC_6H_4CH_2CR_2NH_2$-2 (R = H (**4f**), Me (**4g**)), which in the case of **3c** or **3d** can not be isolated as it undergoes an intramolecular hydroamination process to afford the tetrahydroisoquinoline **5c** or **5d**, respectively. To prepare the tetrahydroisoquinoline **5b**, it is necessary to heat a mixture of complex **1b** with one equiv of TlOTf. The eight-membered cyclic amidine **7d** is obtained from thermal decomposition of complex *cis*-[Pd{*C,N*-CH(CO_2Et)$CH_2C_6H_4CH_2CR_2NH_2$-2}(CNXy)$_2$]OTf (**8d**), prepared by reaction of **2d-5** with TlOTf and XyNC. The amidinium salt **7e-HOTf** is formed by refluxing in toluene a mixture of **2e-4** and TlOTf. The crystal structures of compounds **2a**·$CHCl_3$, **2b-1**,

2d-3·1/3CH_2Cl_2, **2e-4**·1/2$CHCl_3$, **3d**, **3g**, **6** and **7e-HOTf** have been determined by X-ray diffraction studies.

Introduction

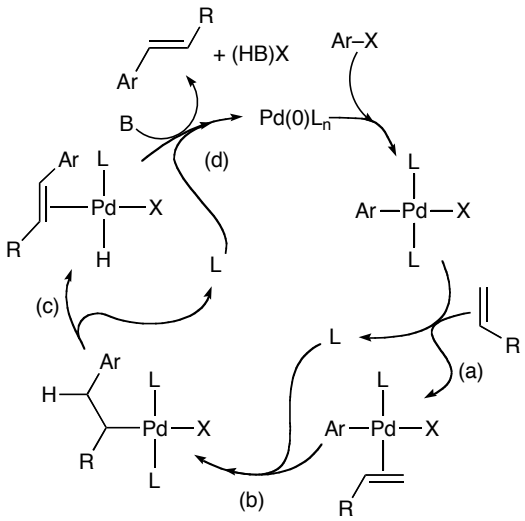
Insertion of olefins into the Pd–C bond of C^N palladacycles derived from tertiary amines,[1-10] imines,[5,8,11,12] oxazolines,[13] pyridines,[4,14] and amides[9,15,16] have been widely investigated because of their applications in organic synthesis. When starting from ortho-palladated secondary or tertiary benzylamines, the reactions give, in most cases, Pd(0) and the products of the Heck reaction, i.e., the ortho-vinylidated amines.[1,5] Instead, we report here that some olefins insert into the Pd–C bond of ortho-palladated primary amines giving stable alkyl palladium compounds that can be decomposed to afford complexes containing coordinated the corresponding ortho-vinylidated amine; when these ligands are replaced, some can be isolated but others undergo a cyclization process through a hydroamination reaction affording tetrahydroisoquinolines. As far as we are aware, the latter behavior has only one precedent that involve a non-isolated ortho-palladated compound.[17]

Scheme 1. Schematic Representation of Some Reactions Studied in this Work



In this study we have used ortho-palladated complexes of the important drugs phenethylamine[18] and phentermine[19] in order to ortho-functionalize them with a vinyl group (Scheme 1). We have previously used the same or similar ortho-palladated complexes[20] of pharmaceutical products to ortho-functionalize them (with Br,[21] I[19,21]) or to form cycles involving the ortho-carbon, an unsaturated molecule (CO,[21] RNC[22,23]) and the nitrogen atom. The interest of this type of research stands on the potential use of these organic compounds or some of their derivatives. Thus, recently, 2-I-tryptophan methyl ester obtained following our method[19] has been used for the total synthesis of the enantiopure alkaloid phalarine.[24]

Scheme 2. Schematic Representation of the Classic Catalytic Cycle for the Heck-Mizoroki Reaction



The group of reactions we have studied are closely related to the Heck-Mizoroki olefin arylation reaction, which is one of the best studied catalytic systems (Scheme 2).[25-29] However, our non-cyclic system differs from the Heck catalytic cycle in two aspects: 1) it lacks the oxidative addition step and 2) the NH_2 group and the halogen atom of the cyclopalladated complexes perform the role of the ligand L required to complete the coordination sphere of Pd in the Heck cycle. The latter difference is responsible of the

different behavior found in some reactions with regard to those in the Heck process, which will be discussed below.

Whereas organometallic complexes arising from insertion of CO,[30-32] RNC,[10,22,23,31,33,34] alkynes[30,32,35,36] and allenes[37] into the Pd–C bond of *C*,*N*-palladacycles have been isolated,[38-40] no complexes emerging from alkene insertion have been reported, although they have been postulated as intermediates in the stoichiometric and catalytic ortho olefination of *N*,*N*-disubstituted arylalquilamines.[3,9,41] In general, Pd(II) complexes with alkyl ligands containing *β*-hydrogens quickly decompose by a *β*-hydride elimination process (Scheme 2, (c))[28,42,43] occurring by a cisoid metal/C–H(*β*) group interaction. Therefore, some of these complexes are stable if this interaction can not be achieved because (1) firmly bound ligands around the Pd atom (for example, a chelating C^N palladacycle and a diphosphine[44] or a C^O palladacycle and a diimine,[45] RNC[45] or phosphine[46-48] ligand) do not allow the generation of the required vacant on the Pd atom or (2) the *β*-hydrogens are inaccessible.[49] Some Pd(II) complexes here reported, containing alkyl ligands with *β*-hydrogens (derived from CH_2=CHC(O)R, R = Me, OEt) are the first compounds stable enough to be isolated in spite of not fulfilling any of the two mentioned stability conditions because the *β*-hydrogens belong to a methylene group within an eight-membered ring (i.e., they are conformationally accessible) and they contain one bridging halide ligand coordinated to the metal (i.e., there is a coordination position not blocked).

In addition, we also show (1) that some changes in the nature of the olefin have a destabilizing effect on the insertion product, e.g., the replacement of (1a) CO_2Et by Ph does not allow to isolate the alkyl complex, and the arylated olefin coordinated to Pd is formed instead and (1b) the olefins CH_2=CHC(O)R (R = Me, OEt) by norbornene give the expected very stable alkyl complexes; (2) that mononuclear derivatives obtained by cleavage of the

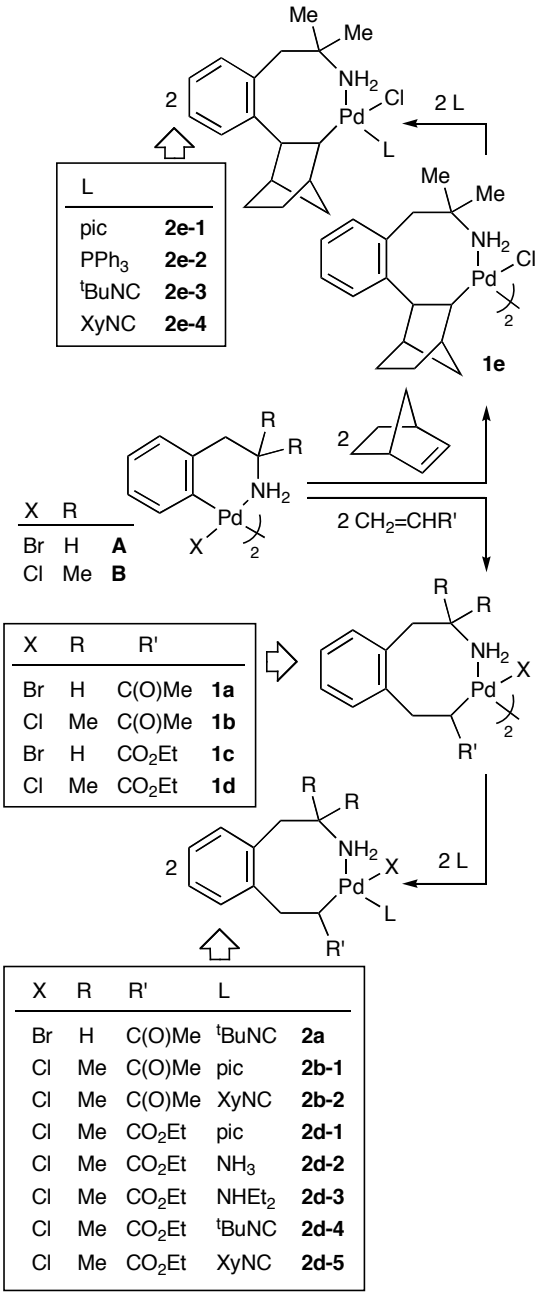
halogen bridge of the insertion products with neutral ligands are more stable than their parent complexes because the entering ligand blocks the coordination site necessary for the *β*-hydrogen elimination, although some derivatives containing XyNC can be decomposed through a C–N coupling process; (3) that replacing the chloride bridges by the weakly bonded triflate anion (OTf) has the contrary effect, because it facilitates the *β*-hydrogen elimination; and (4) that although some arylated olefins can be isolated (R = Ph), when R = C(O)Me or CO_2Et an intramolecular hydroamination occurs giving the corresponding tetrahydroisoquinolines.

Results and Discussion

Synthesis, Structure and Reactivity towards Neutral Ligands of Eight-membered Palladacycles. Ortho-metalated complexes derived from phenethylamine and phentermine $[Pd(C,N\text{-}C_6H_4CH_2CR_2NH_2\text{-}2)(\mu\text{-}X)]_2$ (R = H, X = Br (**A**);[50] R = Me, X = Cl (**B**);[51] Scheme 3) react with olefins CH_2=CHR' or norbornene (C_5H_8) in a 1:2 molar ratio at room temperature, to give dimeric complexes $[Pd\{C,N\text{-}CH(R')CH_2C_6H_4CH_2CR_2NH_2\text{-}2\}(\mu\text{-}X)]_2$ (R = H, X = Cl, R' = C(O)Me (**1a**), CO_2Et (**1c**); R = Me, X = Cl, R' = C(O)Me (**1b**), CO_2Et (**1d**)) and $[Pd\{C,N\text{-}CH(C_5H_8)CHC_6H_4(CH_2CMe_2NH_2)\text{-}2\}(\mu\text{-}Cl)]_2$ (**1e**), respectively, which contain eight-membered palladacycles arising from the insertion of one molecule of alkene into the Pd–C bond. There are only a few eight-membered *C*-palladacycles reported in the literature, arising from insertion of one molecule of alkyne into the Pd–C bond of a six-membered ring,[36,52] or containing chelating bis(diaminocarbene) ligands.[53] Complexes **1a**, **1c** and **1d** are soluble in CH_2Cl_2, whereas **1b** and **1e** precipitate out the reaction mixture. The ^1H spectra in $CDCl_3$ of soluble complexes **1a**, **1b** and **1d** are difficult to analyze because of the existence of various isomers arising from the presence of two chiral centers and the relative position of the

C,N-chelated ligands (*cisoid* and *transoid* isomers). However, their ^{1}H NMR spectra in DMSO-d_6 become simpler probably because the solvent splits the bridges leading to mononuclear species.[54] In all cases, only one set of signals is observed, which means that the insertions and the cleavage of bridges are regiospecific (see below). Similarly, **1a**, **1b**, **1d** or **1e** reacts with a neutral ligand in a 1:2 molar ratio to give only one mononuclear derivative [Pd{*C,N*-CH(R')$CH_2C_6H_4CH_2CR_2NH_2$-2}X(L)] (X = Br, R = H, R' = C(O)Me, L = ^{t}BuNC (**2a**); X = Cl, R = Me, L = 4-methylpyridine (pic), R' = C(O)Me, (**2b-1**), XyNC (**2b-2**); X = Cl, R = Me, R' = CO_2Et, L = pic (**2d-1**), NH_3 (**2d-2**), $NHEt_2$ (**2d-3**), ^{t}BuNC (**2d-4**), XyNC (**2d-5**) or [Pd{*C,N*-CH(C_5H_8)$CHC_6H_4CH_2CMe_2NH_2$-2}Cl(L)] (L = pic, **2e-1**; PPh_3, **2e-2**; ^{t}BuNC, **2e-3**; XyNC, **2e-4**; Scheme 3).

Scheme 3. Synthesis of Eight-membered Palladacycles Derived from Insertion of Methyl Vinyl Ketone, Ethyl Acrylate and 2-Norbornene into the Pd–C Bond of Ortho-metalated Primary Phenethylamines



L	
pic	**2e-1**
PPh_3	**2e-2**
^tBuNC	**2e-3**
XyNC	**2e-4**

X	R	
Br	H	**A**
Cl	Me	**B**

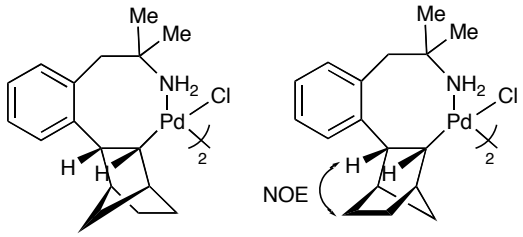
X	R	R'	
Br	H	C(O)Me	**1a**
Cl	Me	C(O)Me	**1b**
Br	H	CO_2Et	**1c**
Cl	Me	CO_2Et	**1d**

X	R	R'	L	
Br	H	C(O)Me	^tBuNC	**2a**
Cl	Me	C(O)Me	pic	**2b-1**
Cl	Me	C(O)Me	XyNC	**2b-2**
Cl	Me	CO_2Et	pic	**2d-1**
Cl	Me	CO_2Et	NH_3	**2d-2**
Cl	Me	CO_2Et	$NHEt_2$	**2d-3**
Cl	Me	CO_2Et	^tBuNC	**2d-4**
Cl	Me	CO_2Et	XyNC	**2d-5**

In agreement with the proposed structures, the ^1H NMR spectra of monomeric complexes **2** show the inequivalence of the NH_2 and CH_2 protons and CMe_2 methyl groups, caused by the presence of one or several chiral centers in the molecule (see ^1H NMR Tables in the SI). For derivatives containing inserted methyl vinyl ketone or ethyl acrylate, the methine hydrogen atom is on C^{α}, which is the most frequent regioisomer found in the insertion of electron-poor alkenes into the Pd–C bonds of neutral complexes.[3,27,29,38,41,55] We propose for

all 2-norbornene derivatives structures arising from the syn addition of the Pd–C bond to the exo face of the olefin (Chart 1) as we have established this geometry in **2e-1** by a NOESY 2D experiment (H^{α} and H^{β} show NOEs to the signals of the hydrogen atoms of the ethylene bridge) and in **2e-4**·1/2$CHCl_3$ (see below) through the resolution of its crystal structure (see below). This is also the geometry observed for similar cases.[26,27,56,57]

Chart 1. Isomers Arising From Insertion of 2-Norbornene into the Pd–C Bond of Six-membered Palladacycles



The crystal structures of complexes **2a**·$CHCl_3$, **2b-1**, **2d-3**·1/3CH_2Cl_2 and **2e-4**·1/2$CHCl_3$ have been solved by X-ray diffraction studies (Figures 1–4) confirming the proposed regiochemistry of the insertion reactions. For complexes **2b-1** and **2d-3**·1/3CH_2Cl_2 there are two and three independent molecules in the asymmetric unit, respectively. In all these complexes the palladium atom is in a slightly distorted square-planar environment. Taking into account the eight internal torsion angles,[58] the metal forms part of an eight-membered ring that adopts a boat-chair (**2b-1**, **2d-3**·1/3CH_2Cl_2, **2e-4**·1/2$CHCl_3$) or a twist-boat-chair (**2a**·$CHCl_3$) conformation. For the other complexes we assume that the monodentated ligands are also placed in trans position to the NH_2 group. For **2e-2** and the isocyanide derivatives, this is the expected geometry because of the great transphobia between C-/C-donor and C-/P-donor pairs of ligands.[34,59]

In complexes **2a**, **2b-1** and **2d-3**, there is an intramolecular hydrogen bond between the oxygen atom of the carbonyl group and one of hydrogen atoms of the NH_2 group while the other is hydrogen bonded to the carbonyl group of another molecule giving rise to dimers. In complex **2b-1**, the dimers are formed between the two independent molecules of the asymmetric unit. In addition, the dimers are further associated through non-classical hydrogen bonds involving aromatic hydrogens and the chloro ligands to give a tridimensional structure.

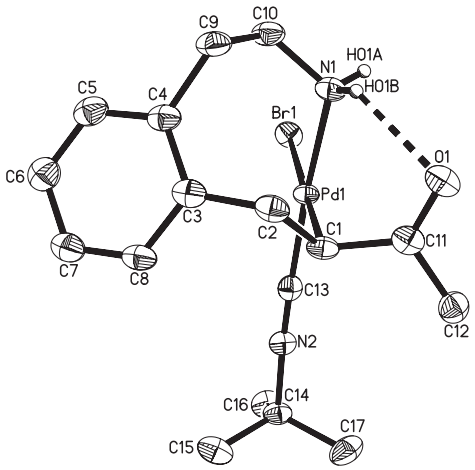


Figure 1. X-ray thermal ellipsoid plot (50% probability) of complex **2a**·$CHCl_3$ showing the labeling scheme (solvent molecule and hydrogen atoms bonded to carbon have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Pd(1)–C(1) = 2.098(2), Pd(1)–N(1) = 2.088(2), Pd(1)–Br(1) = 2.5201(3), Pd(1)–C(13) = 1.931(3); C(1)–Pd(1)–N(1) = 90.61(9), N(1)–Pd(1)–Br(1) = 87.55(6), Br(1)–Pd(1)–C(13) = 95.00(7), C(13)–Pd(1)–C(1) = 86.86(10).

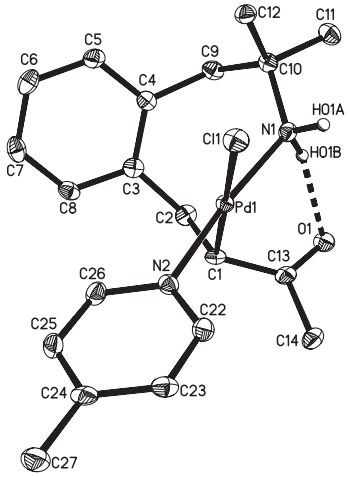


Figure 2. X-ray thermal ellipsoid plot of one (A) of the two independent molecules of complex **2b-1** (50% probability) showing the labeling scheme (hydrogen atoms bonded to carbon have been omitted for clarity). Selected bond lengths (Å) and angles (deg) are given for both independent molecules. For A: Pd(1)–N(1) = 2.067(2), Pd(1)–N(2) = 2.039(2), Pd(1)–C(1) = 2.097(3), Pd(1)–Cl(1) = 2.3894(7); C(1)–Pd(1)–N(1) = 89.94(10), N(1)–Pd(1)–Cl(1) = 93.01(7), Cl(1)–Pd(1)–N(2) = 87.02(7), N(2)–Pd(1)–C(1) = 89.91(10), Pd(1)–C(1)–C(2) = 113.20(18). For B: Pd(2)–N(3) = 2.060(2), Pd(2)–N(4) = 2.036(2), Pd(2)–C(31) = 2.102(3), Pd(2)–Cl(2) = 2.3947(7); C(31)–Pd(2)–N(3) = 90.15(10), N(3)–Pd(2)–Cl(2) = 92.33(7), Cl(2)–Pd(2)–N(4) = 87.97(7), N(4)–Pd(2)–C(31) = 89.37(10), Pd(2)–C(31)–C(32) = 114.74(18).

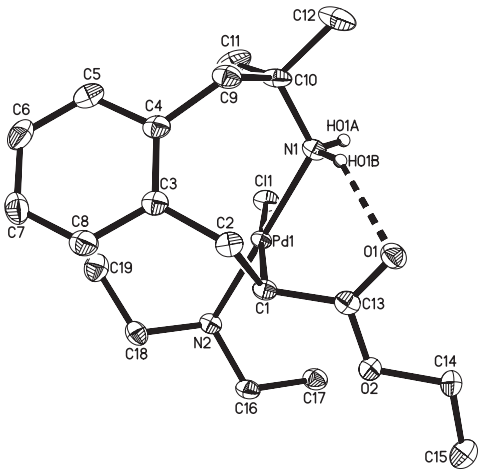


Figure 3. X-ray thermal ellipsoid plot of one (A) of the three independent molecules of complex **2d-3**·1/3CH_2Cl_2 (50% probability) showing the labeling scheme (solvent molecules and hydrogen atoms bonded to carbon have been omitted for clarity). Selected bond lengths (Å) and angles (deg) are given for the three independent molecules. For A: Pd(1)–N(1) = 2.064(2), Pd(1)–N(2) = 2.084(2), Pd(1)–C(1) = 2.078(2), Pd(1)–Cl(1) = 2.4250(6); C(1)–Pd(1)–N(1) = 90.81(9), N(1)–Pd(1)–Cl(1) = 92.34(6), Cl(1)–Pd(1)–N(2) = 84.59(6), N(2)–Pd(1)–C(1) = 92.27(9), Pd(1)–C(1)–C(2) = 116.47(17). For B: Pd(1')–N(1') = 2.071(2), Pd(1')–N(2') = 2.084(2), Pd(1')–C(1') = 2.069(2), Pd(1')–Cl(1') = 2.4368(6); C(1')–Pd(1')–N(1') = 90.67(9), N(1')–Pd(1')–Cl(1') = 91.84(6), Cl(1')–Pd(1')–N(2') = 85.58(6), N(2')–Pd(1')–C(1') = 92.21(9), Pd(1')–C(1')–C(2') = 116.78(16). For C: Pd(1")–N(1") = 2.067(2), Pd(1")–N(2") = 2.086(2), Pd(1")–C(1") = 2.082(2), Pd(1")–Cl(1") = 2.4102(6); C(1")–Pd(1")–N(1") = 91.06(9), N(1")–Pd(1")–Cl(1") = 90.20(6), Cl(1")–Pd(1")–N(2") = 86.53(6), N(2")–Pd(1")–C(1") = 92.27(9), Pd(1")–C(1")–C(2") = 116.36(16).

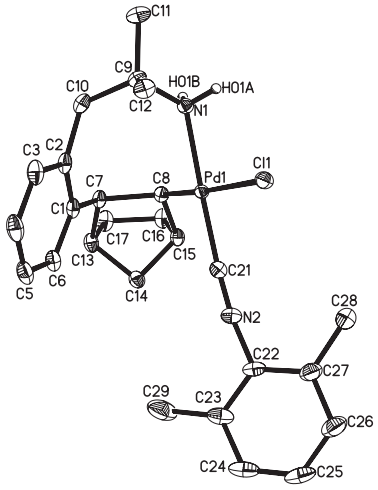


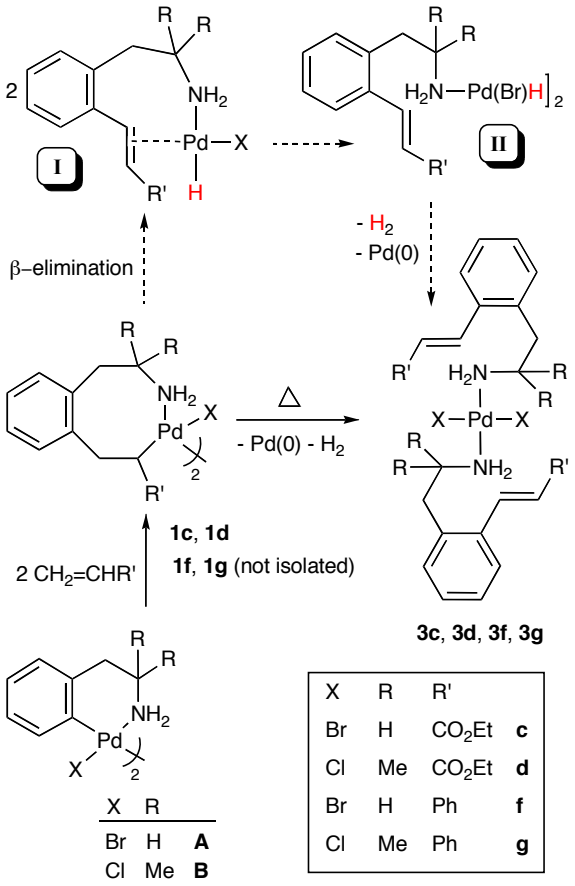
Figure 4. X-ray thermal ellipsoid plot of complex **2e-4**·1/2$CHCl_3$ (50% probability) showing the labeling scheme (solvent molecules and hydrogen atoms bonded to carbon have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Pd(1)–N(1) = 2.0961(17),

Pd(1)–Cl(1) = 2.4463(5), Pd(1)–C(21) = 1.928(2), Pd(1)–C(8) = 2.053(2); N(1)–Pd(1)–Cl(1) = 89.77(5), Cl(1)–Pd(1)–C(21) = 88.81(6), C(21)–Pd(1)–C(8) = 94.18(8), C(8)–Pd(1)–N(1) = 87.14(7), Pd(1)–C(8)–C(7) = 116.34(13).

Study of the Stability of Complexes 1 and 2. **Synthesis of Tetrahydroisoquinolines and 2-Ortho-vinylidated Phenethylamines.** In the solid state at room temperature, these complexes remain unaltered for long periods of time. In solution, complexes **1a**, **1c** and **1d** are stable in DMSO for days, whereas complexes **1c** and **1d** start to decompose after 4 h in $CHCl_3$. All mononuclear complexes are stable except the norbornene derivatives **2e-1** and **2e-2** (see below). The stability of complexes derived from the carbonyl-olefins is noteworthy because the eight-membered metallacycles are not conformationally rigid and Pd(II) has one easily available coordination site through the halide bridge, i.e., they do not fulfill none of the two stability conditions established for Pd(II) complexes with alkyl ligands containing *β*-hydrogens to prevent quick decomposition by a *β*-hydride elimination process (see Introduction and Scheme 1, steps (c) and (d)).[28,42,43,45,47,48,57,60] Three factors could contribute to this behavior: (1) the Pd–NH_2 bond strength, since reactions of olefins (including those used by us) with *N*,*N*-disubstituted benzylamines do not afford the homologues of complexes **1**, but the arylated olefins resulting from their decomposition, in spite of the potential stabilizing effect of the seven membered ring formed;[3,9,41] (2) the presence of an electron-withdrawing substituent on the *α*-carbon,[61] since the alkyl Pd(II) intermediate is not isolated in the reaction with styrene (see below); and (3) the flexibility of the eight-membered palladacycle could be somehow restricted by the presence in solution of the intramolecular hydrogen bond we observe in the solid state (Figures 1–3); this stabilizing effect would not be present in the case of the styrene insertion either.

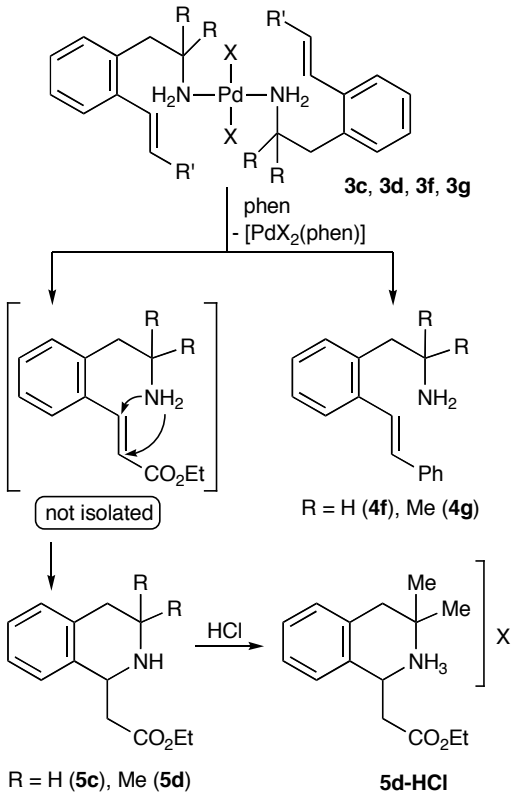
Complexes **1** and **2**, except **2e** derived from norbornene, are actual models for the proposed alkyl complex intermediate in the Heck-Mizoroki catalytic process[3,9,39,41,43,62] because they can be decomposed to give the arylated olefins. Thus, when a solution of **1c** (CH_2Cl_2, 45 ºC) or **1d** ($CHCl_3$, 60 ºC) is stirred for 12 or 7 h, respectively, the coordination complex containing as ligand the arylated olefin *trans*-[$PdX_2(NH_2CR_2CH_2C_6H_4CH{=}CHCO_2Et\text{-}2)_2$] (R = H, X = Cl (**3c**); R = Me, X = Br (**3d**)) is obtained in 60–70% yield along with metallic palladium (Scheme 4). Analogous complexes **3f** (R' = Ph, R = H, X = Cl) or **3g** (R' = Ph, R = Me, X = Br) can be obtained by reacting palladacycles **A** or **B** with styrene in a 1:2 molar ratio, although in this case, it is not possible to isolate the eight-membered palladacycle **1f** or **1g**, respectively. As far as we are aware, this is the first work reporting that the arylated olefins formed from the insertion of an alkene and a β-reductive elimination process are trapped as ligands by Pd(II).

Scheme 4. Decomposition of Dimeric Complexes Derived from the Insertion of Ethyl Acrylate and Styrene



A possible mechanism for the decomposition reactions of complexes **1** to give complexes **3** involve: 1) *β*-hydrogen elimination to give an η^2-olefin-hydrido-complex of Pd(II) (**I**; Scheme 4), 2) formation of a dinuclear intermediate (**II**), and 3) disproportionation of **II** to give H_2, Pd(0) and complex **3**. This step is different from that postulated in the Heck catalytic cycle (Scheme 2),[3,5-7,9-11,14,16,48] probably because of the existence in our case of the NH_2–Pd strong bond. We have previously obtained similar complexes in the decomposition of [Pd{C(=NXy)$C_6H_4CH_2NH_2$-2}Br(CNXy)] to give [$PdBr_2${2-(XyNH)isoindole}$_2$], Pd(0) and H_2, or in the halogenation of [Pd_2(*C*,*N*-$C_6H_4CH_2CMe_2NH_2$-2)$_2$(μ-Cl)$_2$] or (*S*,*S*)-[Pd_2{*C*,*N*-$C_8H_5NCH_2CH(CO_2Me)NH_2$-2}$_2$($\mu$-Cl)$_2$] to afford [$PdX_2$(L-X')$_2$] (L-X' = ortho-halogenated primary amine) and PdX'_2.[19,21,22]

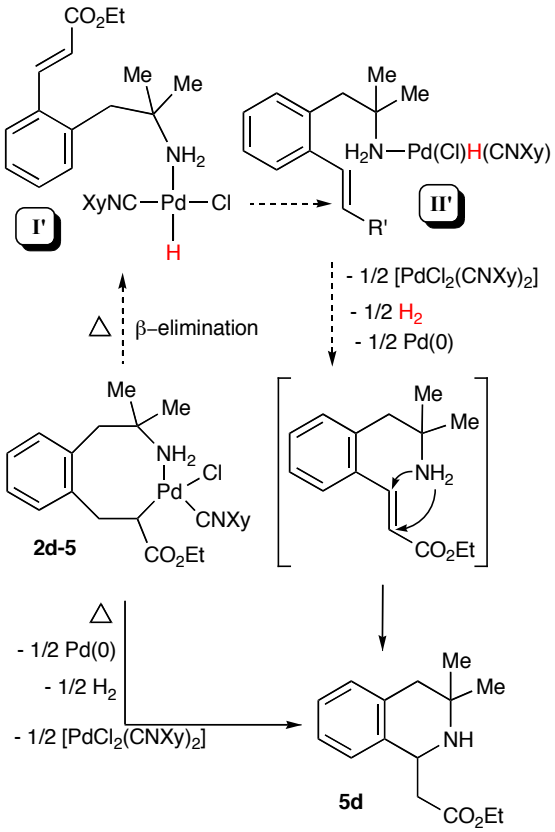
Scheme 5. Synthesis of Vinylidated-amines and Tetrahydroisoquinolines



The reaction of complex **3f** or **3g** with 1,10-phenanthroline·H_2O (phen) led to [PdX_2(phen)] (X = Cl or Br) and the free ortho-vinylidated amines 2-styryl-phenethylamine (**4f**) or -phentermine (**4g**; Scheme 5). When the analogous reactions were carried out with complexes **3c** and **3d**, the tetrahydroisoquinolines **5c** and **5d** formed. They must arise from the intramolecular hydroamination of the 2-vinylidated phenethylamine, as its double bond is activated by the presence of an electron-withdrawing group.[7,17,63] Therefore, complexes **3c** and **3d** contain short-lived species as ligands. Protonation of **5d** with HCl afforded **5d**-HCl. **5d** was also obtained, along with Pd(0) and [$PdCl_2(CNXy)_2$], when complex **2d-5** was refluxed in toluene, which means that **5d** is not nucleophilic enough to attack the coordinated XyNC ligand. The reaction that affords **5d** probably follows an analogous pathway to that proposed for the decomposition of palladacycle **1d** (Scheme 4), but the presence of the isocyanide must generate different intermediates (Scheme 6). Thus, for example, formation of the intermediate **I'** will require, probably, the previous dissociation of the chloro ligand to

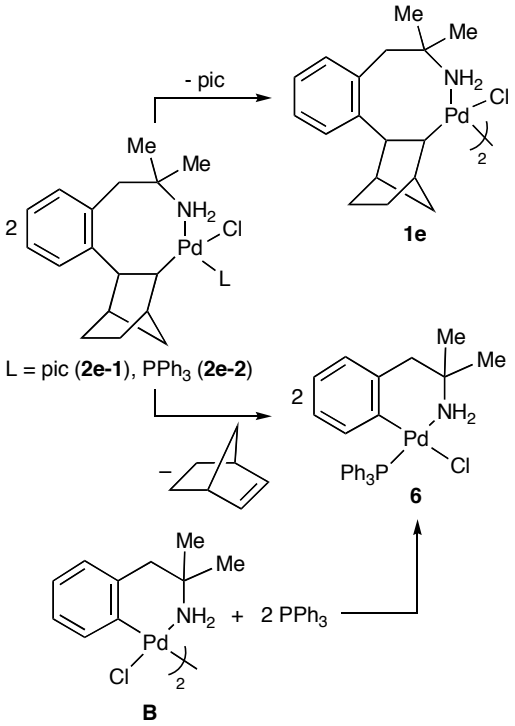
allow the *β*-hydrogen migration; decomposition of **II'** will not lead to **3d** because this would involve the dissociation of XyNC instead of the amine.

Scheme 6. Proposed Mechanism for the Thermal Decomposition of **2d-5**.



Complexes **1e** and **2e**, derived from 2-norbornene insertion, did not decompose through *β*-hydride elimination, as the palladium and the *β*-hydrogen atom cannot adopt the needed mutually syn disposition. Instead, at room temperature, complex **2e-1** loses 4-picoline in solution to regenerate **1e**, while **2e-2** undergoes extrusion of 2-norbornene to give [Pd{*C,N*-CH(R')$CH_2C_6H_4CH_2CR_2NH_2$-2}Cl(PPh_3)] (**6**), which can be independently prepared by reaction of the palladacycle **B** and PPh_3 in a 1:2 molar ratio (Scheme 7). Other authors have previously observed 2-norbornene deinsertion from their palladium(II) complexes as a consequence of high steric congestion around the metal center.[64]

Scheme 7. Decomposition of Mononuclear Complexes Derived from the Insertion of 2-Norbornene



In the ^{1}H NMR spectra of compounds **3** and **4** each olefinic hydrogen appears as a doublet, with coupling constants between 15.2 and 16.0 Hz, which is in agreement with the trans geometry of the double bond.

The crystal structures of complexes **3d** and **3g** (Figures 5 and 6) show two centrosymmetric molecules with the palladium atom coordinated to two chloro ligands and the nitrogen atoms of two ortho-vinylidated amines, in an almost perfect square-planar geometry. The amino ligands adopt a mutually trans disposition, which is the normal geometry for bis(amino)-dihalopalladium(II) complexes.[19,32,65] The olefinic double bond shows a trans geometry. In both complexes, the molecules are associated through N–H···Cl hydrogen bonds to give chains along the *a* axis. In complex **3d**, two adjacent chains are connected through a weak interaction between the chloro ligand and one aromatic hydrogen (Figures 7 and 8).

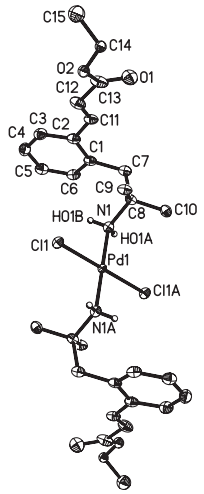


Figure 5. X-ray thermal ellipsoid plot of complex **3d** (50% probability) showing the labeling scheme (hydrogen atoms bonded to carbon have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Pd(1)–N(1) = 2.052(2), Pd(1)–Cl(1) = 2.3000(7), C(11)–C(12) = 1.316(4); N(1)–Pd(1)–Cl(1) = 89.40(7), N(1)–Pd(1)–Cl(1A) = 90.60(7).

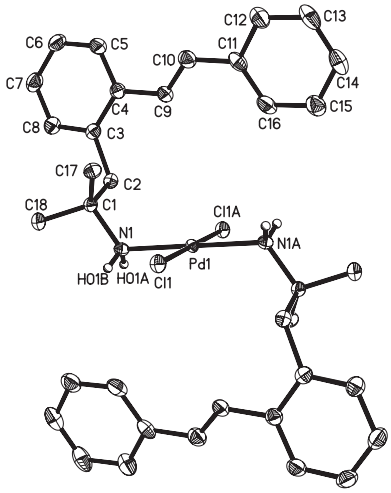


Figure 6. X-ray thermal ellipsoid plot of complex **3g** (50% probability) showing the labeling scheme (hydrogen atoms bonded to carbon have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Pd(1)–N(1) = 2.0638(16), Pd(1)–Cl(1) = 2.2991(5), C(9)–C(10) = 1.339(3); N(1)–Pd(1)–Cl(1) = 87.47(5), N(1)–Pd(1)–Cl(1A) = 92.53(5).

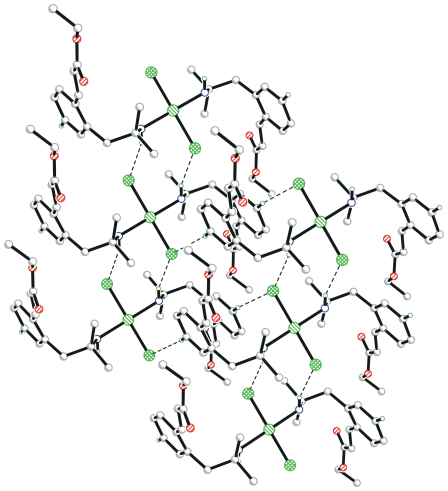


Figure 7. X-ray packing view of complex **3d** showing the double chains along the *a* axis formed through hydrogen bond interactions. Details (including symmetry operators) are given in the Supporting Information.

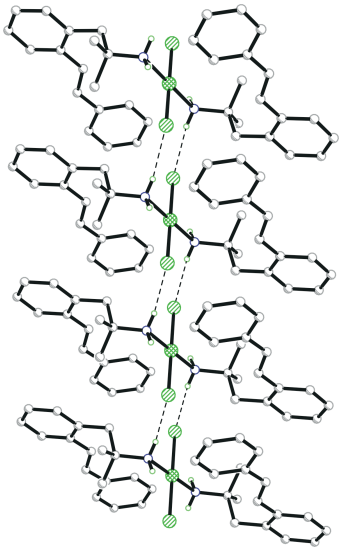


Figure 8. X-ray packing view of complex **3g** showing the chains along the *a* axis formed through hydrogen bond interactions. Details (including symmetry operators) are given in the Supporting Information.

Reported methods of synthesis of **4f** use as starting materials: (1) 2-bromobenzaldehyde, styrene and nitromethane, followed by reduction with $LiAlH_4$ (three

steps, overall yield 49%),[63] and 2) 2-methylbenzaldehyde, benzyltriphenylphosphonium bromide, *N*-bromosuccinimide and sodium cyanide, followed by reduction with $LiAlH_4$ (four steps, 42% overall yield).[66] Our method requires three steps using phenethylamine, $Pd(OAc)_2$, styrene and phenanthroline with an overall yield of 10%. Compound **5c** has been prepared by: 1) condensation of phenylethyl chloride and ethyl cyanoacetate using stannic chloride and hydrogenation of the resulting dihydroisoquinoline (three steps, overall yield 28–35%),[67] 2) reaction of ethyl (*E*)-2-(2-bromoethyl)-cinnamate with potassium phthalimide followed by treatment with hydrazine hydrate (two steps, 63%),[68] or 3) reaction of 3,4-dihydroisoquinoline (prepared from 2-chloroethyl-benzaldehyde and NH_4OH) with malonic acid ethyl ester (two steps, overall yield 74%).[69] Our method requires three steps using phenethylamine, $Pd(OAc)_2$, ethylacrylate and phenanthroline with an overall yield of 16%. To our knowledge, no synthesis of compounds **4g**, **5b** and **5d** have been reported. In our opinion, the main interest of this part of our study is based on (1) the isolation of the stable Heck intermediates **1** and **2**, (2) the synthesis of complexes **3** containing non-existent amines, (3) the observation of the hydroamination of ortho-vinylated-phenethylamines into tetrahydroisoquinolines and (4) the first reported synthesis of **4g**, **5b** and **5d**.

The crystal structure of complex **6** (Figure 9) shows the palladium atom in a distorted square-planar environment. The chelate ligand forms a six-membered palladacycle with a boat conformation. These features are similar to those of analogous complexes containing primary or secondary ortho-metalated phenethylamines.[18,21,32,50,70] The phosphine and the NH_2 group are mutually trans, according to the higher transphobia of the pair of ligands P/C_{Ar} than P/N.[34,59] The molecules form intermolecular H···Cl···H bridging hydrogen bonds between the chloro ligand of one molecule and a Me and a NH hydrogens of another one giving rise to dimers (Figure 10).

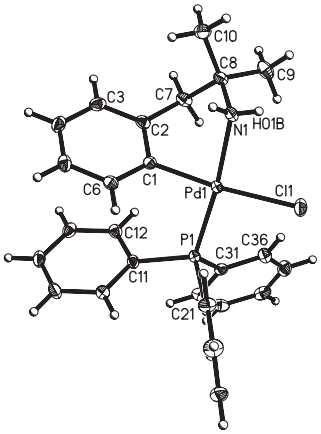


Figure 9. X-ray thermal ellipsoid plot of complex **6** (50% probability) showing the labeling scheme (hydrogen atoms bonded to carbon have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Pd(1)–C(1) = 1.9964(17), Pd(1)–N(1) = 2.1226(16), Pd(1)–Cl(1) = 2.4136(5), Pd(1)–P(1) = 2.2606(5); C(1)–Pd(1)–N(1) = 82.30(7), N(1)–Pd(1)–Cl(1) = 89.98(5), Cl(1)–Pd(1)–P(1) = 96.653(17), P(1)–Pd(1)–C(1) = 91.52(5).

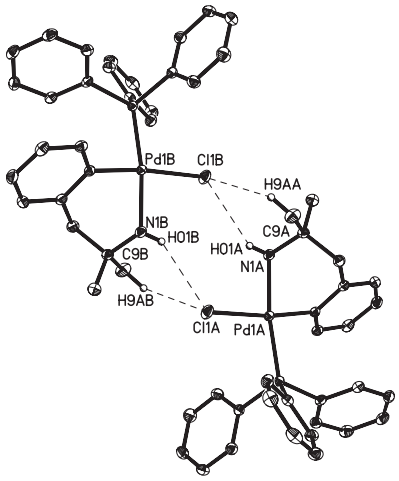
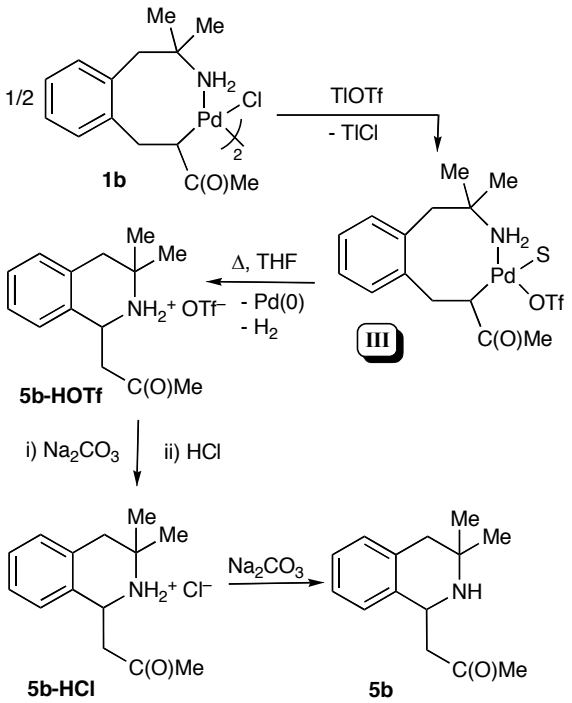


Figure 10. X-ray packing view of complex **6** showing intermolecular H_{Me}···Cl···HN hydrogen bond interactions.

Decomposition of Complexes by Replacement of the Chloro Ligand by Triflato. To generate the required vacant on the Pd atom to allow the *β*-hydrogen elimination there is an alternative way to that used in the thermal decomposition of complex **5d**: the replacement

of the chloro ligand by an easily replaceable one such as triflato. Complex **1b** did not decompose when stirred in $CHCl_3$ at room temperature or when it was treated with a stream of CO, however, when a suspension of **1b** in THF was reacted with TlOTf and refluxed, the corresponding tetrahydroisoquinolonium salt **5b-HOTf** (Scheme 8) was obtained. The impure salt was treated with Na_2CO_3, then with HCl to give the rather hygroscopic isoquinolinium salt **5b-HCl** that was neutralized with Na_2CO_3 to afford pure tetrahydroisoquinoline **5b**, which is easier to manipulate (Scheme 8). In this case, the process is facilitated by the formation of an unstable triflato- or solvento-complex (**III**),[48] which decomposition probably occurs by direct formation the 2-vinylidated phentermine that cyclizes to give **5b-OTf**.

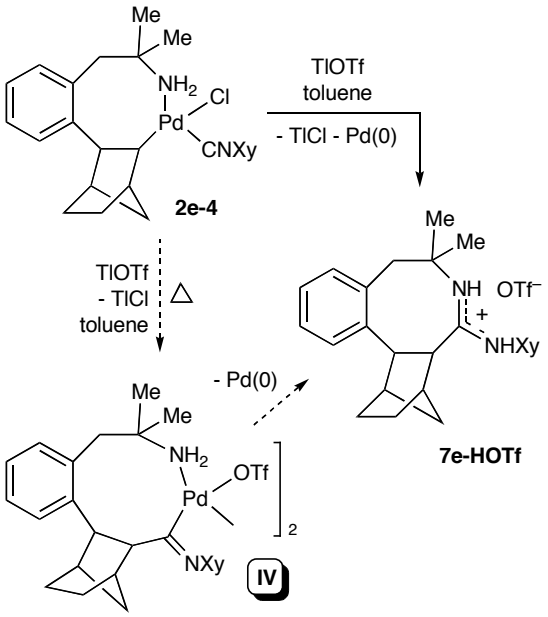
Scheme 8. Decomposition of **1b** in the Presence of Thallium Triflate.



As expected, the replacement of the chloro ligand by triflato in norbornene derivatives did not allow the *β*-hydrogen migration (see Scheme 7), since of the inaccessibility of the *β*-hydrogen still remains. Thus, when the isocyanide complex **2e-4** was reacted with one equiv of TlOTf in refluxing toluene, the eight-membered amidinium salt **7e-HOTf** is obtained

(Scheme 9). Therefore, instead of the *β*-hydrogen migration, the insertion of the isocyanide followed by a reductive C–N coupling is the favored process. We have used this method to prepare other cyclic amidines, although with one less member in the cycle.[21-23] If a similar reaction is carried out starting from complex **2e-3**, containing coordinated ^{t}BuNC, an unidentified compound was obtained as the main product, which showed no ^{t}Bu resonance in its ^{1}H NMR spectrum. A similar behavior has been previously observed by us when trying to prepare the amidinium salt derived from the insertion of ^{t}BuNC into the Pd–C bond of palladacycle **A**.[23]

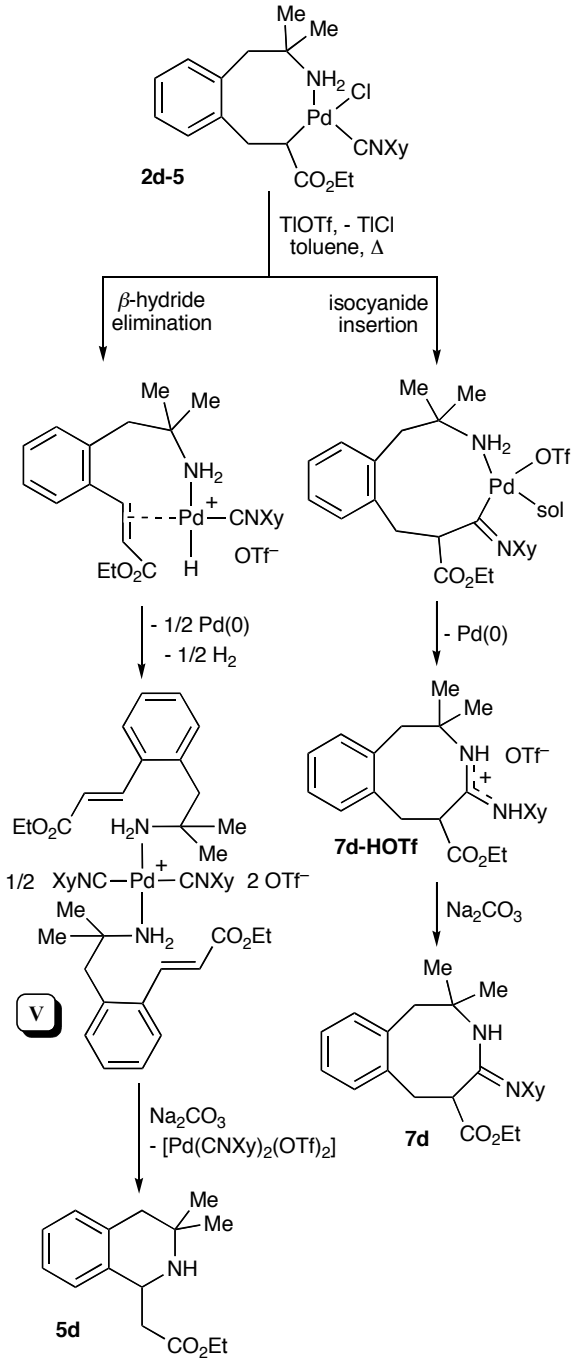
Scheme 9. Decomposition of **2e-4** in Presence of Thallium Triflate. Synthesis of **7e-HOTf**.



We have mentioned above that **2d-5** decomposes when refluxed in toluene affording the tetrahydroisoquinoline **5b** (Scheme 6). If the same reaction is carried out in the presence of one equiv of TlOTf, both *β*-hydrogen elimination and C–N coupling processes are observed simultaneously (Scheme 10). The ^{1}H NMR spectrum of the product resulting after removing Pd(0) and the solvent, showed the presence of the amidinium salt **7d-HOTf** and a

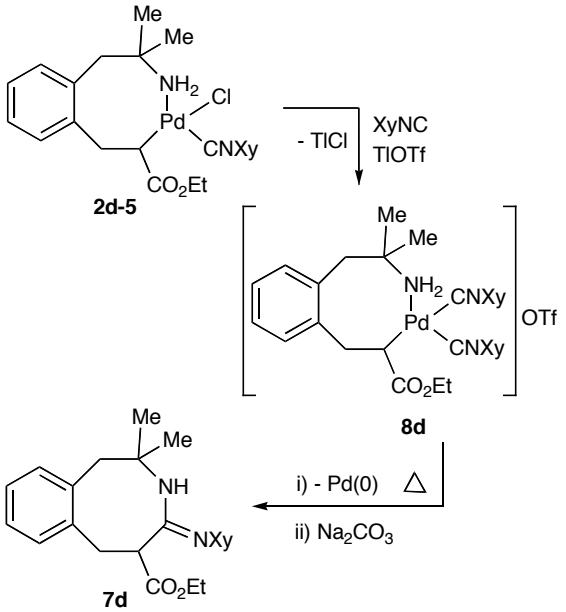
Pd(II)-complex containing the ortho-vinylidated amine (probably, intermediate **V**). The treatment of this residue with Na_2CO_3 afforded a 1:3 mixture of **5d** and the cyclic amidine **7d**.

Scheme 10. Proposed Pathways for the Decomposition of Complex **2d-5** in the Presence of Triflate



In order to favor the isocyanide insertion over the *β*-hydride elimination, we seek to use as starting material a complex with strongly coordinating ligands, that is, a complex where all the coordination positions of Pd(II) were blocked. The reaction of complex **2d-5** with TlOTf and XyNC (molar ratio 1:1:1; Scheme 11) allows the synthesis of the cationic complex *cis*-[Pd{*C,N*-CH(CO_2Et)$CH_2C_6H_4CH_2CR_2NH_2$-2}(CNXy)$_2$]OTf (**8d**). The ^{1}H and ^{13}C NMR data of this complex confirm the proposed structure, as well as its IR spectrum, which shows two strong peaks corresponding to the ν(C≡N) stretching frequencies at 2184 and 2000 cm^{-1}. As designed, when complex **8d** was heated in $CHCl_3$ at 70 ºC in a Carius tube, and the resulting mixture was treated with Na_2CO_3, the amidine **7d** was obtained as a unique product with a 60% isolated yield (Scheme 11). Therefore, depending on the reaction conditions, complex **2d-5** can be decomposed selectively 1) by refluxing it in toluene, to afford the tetrahydroisoquinoline **5d** through a *β*-hydride elimination process (Scheme 6) or 2) by heating it in the presence of TlOTf and XyNC, to give the cyclic amidine **7d** through insertion of XyNC and C–N coupling processes (Scheme 11). When **2d-5** is refluxed in toluene in the presence of TlOTf it decomposes through both pathways (Scheme 10).

Scheme 11. Synthesis and Decomposition of Complex **8d**



The crystal structure of the compound **7e-HOTf** (Figure 11) has been determined by X-ray diffraction studies and it shows a fused eight-membered azacycle with a twist-boat conformation. Additionally, both groups (C1 and C9) at the disubstituted norbornane unit are in an exo disposition, as expected.

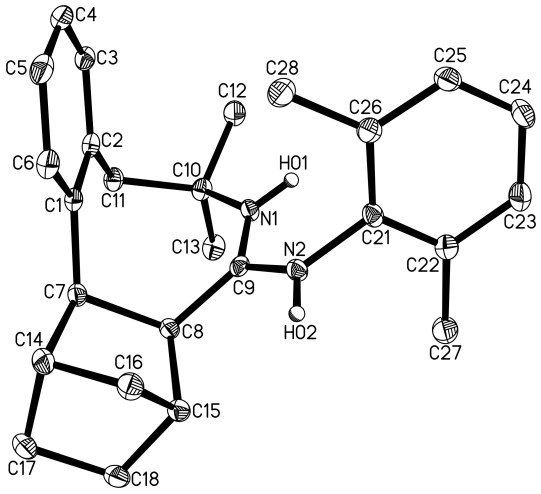


Figure 11. X-ray thermal ellipsoid plot of the cation of compound **7e-HOTf** (50% probability) showing the labeling scheme (hydrogen atoms bonded to carbon have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Pd(1)–N(1) = 2.0638(16),

Pd(1)–Cl(1) = 2.2991(5), C(9)–C(10) = 1.339(3); N(1)–Pd(1)–Cl(1) = 87.47(5), N(1)–Pd(1)–Cl(1A) = 92.53(5).

Conclusion

The insertion of alkenes into the Pd–C bond of ortho-metalated phenethylamines allows the synthesis of stable eight-membered palladacycles bearing one or two *β*-hydrogens. The stability of some of these complexes is surprising as the *β*-hydrogens are conformationally available and at least a halogen ligand coordinated to the metal offers an accessible coordination site for the *β*-hydrogen elimination process. Under various reaction conditions these complexes decompose through a *β*-hydride elimination process to give complexes containing two coordinated ortho-vinylidated arylakylamine - some of which do not exist in the free state - that can be replaced and isolated (styryl derivatives) or spontaneously transformed into tetrahydroisoquinolines (ethyl acrylate derivatives). Replacement of the chloro ligand by triflato can be used to promote decomposition by *β*-hydrogen elimination (methyl vinyl derivatives) or to insert isocyanides affording cyclic amidine derivatives. We also show (1) that some changes in the nature of the olefin have a destabilizing effect on the insertion product, e.g., (1a) the replacement of CO_2Et by Ph does not allow to isolate the alkyl complex, and the arylated olefin coordinated to Pd is formed instead and (1b) the change of olefins CH_2=CHC(O)R (R = Me, OEt) by norbornene gives the expected very stable alkyl-complexes and (2) that mononuclear derivatives obtained by cleavage of the halogen bridge of the insertion products with neutral ligands are more stable than their parent complexes because the entering ligand blocks the coordination site necessary for the hydrogen elimination, although some derivatives containing XyNC can be decomposed through a C–N coupling process.

Experimental Section

General Procedures. Infrared and NMR spectra, C, H, N and S analyses, conductance measurements, and melting point determinations were carried out as described elsewhere.[32] Unless otherwise stated, reactions were carried out at room temperature and without special precautions against moisture.

The ortho-metalated complexes $[Pd_2\{C,N\text{-}C_6H_4CH_2CH_2NH_2\text{-}2\}_2(\mu\text{-}Br)_2]$ (**A**)[50] and $[Pd_2\{C,N\text{-}C_6H_4CH_2CMe_2NH_2\text{-}2\}_2(\mu\text{-}Cl)_2]$ (**B**)[51] were prepared as previously reported. Ethyl acrylate (Merck), styrene (Aldrich), methyl vinyl ketone, 2-norbornene, 4-methylpyridine (4-picoline), $NHEt_2$, PPh_3, ^tBuNC, XyNC, HOTf (HSO_3CF_3) (Fluka), NH_3 (gas, Air Products) and palladium acetate (Johnson Matthey) were used as received. TlOTf ($TlSO_3CF_3$) was prepared by reaction of Tl_2CO_3 and HSO_3CF_3 (1:2) in water and recrystallized from acetone/Et_2O. Chart 2 gives the numbering schemes for the six- and eight-membered palladacycles, ortho-vinylated phenethylamines and N-heterocycles.

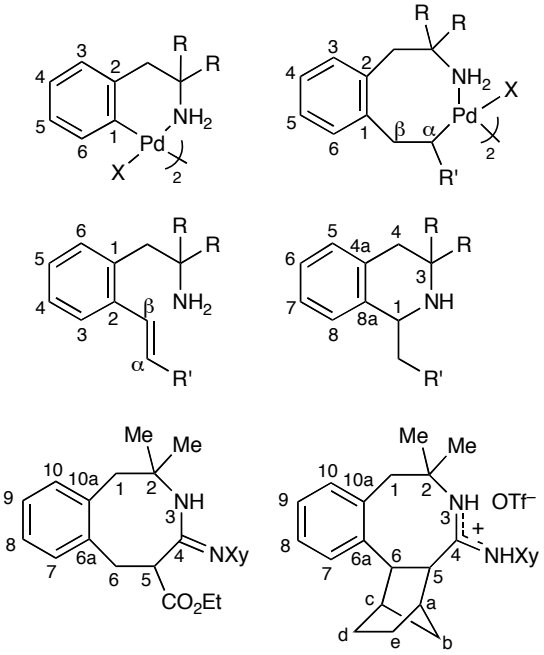


Chart 2. Numbering Schemes for Six- and Eight-membered Palladacycles, Ortho-vinylated Phenethylamines, Tetrahydroisoquinolines, Amidines and Amidinium Salts

Synthesis of [Pd$_2${*C,N*-CH(COMe)CH$_2$C$_6$H$_4$(CH$_2$CH$_2$NH$_2$)-2}$_2$(μ-Br)$_2$] (1a). Methyl vinyl ketone (0.058 mL, 0.693 mmol) was added to a solution of complex [Pd$_2${*C,N*-C$_6$H$_4$CH$_2$CH$_2$NH$_2$-2}$_2$(μ-Br)$_2$] (**A**; 200 mg, 0.326 mmol) in CH_2Cl_2 (10 mL). The resulting mixture was stirred for 2 h and then filtered through a plug of Celite. The filtrate was concentrated to ca. 2 mL, and Et_2O (20 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give complex **1a** as an orange solid. Yield: 191 mg, 0.253 mmol, 78%. Dec pt: 130 °C. Anal. Calcd for $C_{24}H_{32}Br_2N_2O_2Pd_2$ (753.172): C, 38.27; H, 4.28; N, 3.72. Found: C, 38.40; H, 4.37; N, 3.81. IR (cm^{-1}): ν(NH) 3205 s, 3126 vs; ν(CO) 1610 vs. ^{1}H NMR (DMSO-d_6, 400.91 MHz): δ 2.06 (m, partially obscured by the methyl resonance, 1 H, C$^{\beta}$H$_2$), 2.09 (s, 3 H, Me), 2.11–2.20 (m, 1 H, NH$_2$), 2.70 (d, 1 H, CH$_2$Ar, $^2J_{HH}$ = 14.0 Hz), 2.97–3.17 (m, 3 H, 1 H of CH$_2$Ar + 2 H of CH$_2$N), 3.34 (m, partially obscured by the signal corresponding to traces of H_2O in the deuterated solvent, 1 H, C$^{\beta}$H$_2$), 4.14 (dd, 1 H, C$^{\alpha}$H, $^3J_{HH}$ = 11.2, $^3J_{HH}$ = 6.4 Hz), 4.93 (d, 1 H, NH$_2$, $^2J_{HH}$ = 10.8 Hz), 7.16 (d, 1 H, H6, $^3J_{HH}$ = 7.6 Hz), 7.20–7.30 (m, 3 H, H3 + H4 + H5). ^{13}C{^{1}H} NMR (DMSO-d_6, 100.81 MHz): δ 28.8 (s, Me), 30.4 (s, C$^{\beta}$H$_2$), 32.4 (s, CH$_2$Ar), 47.6 (s, CH$_2$N), 54.4 (s, C$^{\alpha}$H), 126.2 (s, CH, C4), 126.7 (s, CH, C5), 128.6 (s, CH, C6), 130.6 (s, CH, C3), 137.5 (s, C2), 141.0 (s, C1), 203.1 (s, CO).

Synthesis of [Pd$_2${*C,N*-CH(COMe)CH$_2$C$_6$H$_4$(CH$_2$CMe$_2$NH$_2$)-2}$_2$(μ-Cl)$_2$]·1/4CH$_2$Cl$_2$ (1b·1/4CH$_2$Cl$_2$). Methyl vinyl ketone (0.060 mL, 0.717 mmol) was added to a suspension of complex [Pd$_2${*C,N*-C$_6$H$_4$CH$_2$CMe$_2$NH$_2$-2}$_2$(μ-Cl)$_2$] (**B**; 200 mg, 0.345 mmol) in CH_2Cl_2 (5 mL) and the resulting mixture was stirred for 1 h. A yellow solid precipitated,

which was collected by filtration, washed with a 1:1 mixture of CH_2Cl_2 and Et_2O (4 mL) and Et_2O (10 mL) and air-dried to give complex **1b**·1/4CH_2Cl_2 as a yellow solid. Yield: 176 mg, 0.237 mmol, 69%. Mp: 130 °C dec. Anal. Calcd for $C_{28}H_{40}Cl_2N_2O_2Pd_2$·1/4$CH_2Cl_2$ (741.609): C, 45.75; H, 5.50; N, 3.77. Found: C, 45.88; H, 5.84; N, 3.86. IR (cm^{-1}): ν(NH) 3190 s, 3125 s; ν(CO) 1605 s. ^{1}H NMR (DMSO-d_6, 400.91 MHz): δ 1.14 (s, 3 H, Me, CMe_2), 1.37 (s, 3 H, Me, CMe_2), 1.98 (dd, 1 H, C$^{\beta}$H$_2$, $^2J_{HH}$ = 13.6, $^3J_{HH}$ = 7.2 Hz), 2.11 (s, 3 H, MeCO), 2.29 (d, 1 H, NH_2, $^2J_{HH}$ = 12.0 Hz), 2.46 (d, one-half of the doublet was obscured by the DMSO signal, 1 H, CH_2Ar), 3.20 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.0 Hz), 3.31 (m, partially obscured by the signal corresponding to traces of H_2O in the deuterated solvent, 1 H, C$^{\beta}$H$_2$), 4.12 (dd, 1 H, C$^{\alpha}$H, $^3J_{HH}$ = 10.8, $^3J_{HH}$ = 7.2 Hz), 4.69 (d, 1 H, NH_2, $^2J_{HH}$ = 11.6 Hz), 5.74 (s, CH_2Cl_2), 7.16 (m, 2 H, H3 + H6), 7.21 (t, 1 H, H4, $^3J_{HH}$ = 7.6 Hz), 7.30 (t, 1 H, H5, $^3J_{HH}$ = 7.2 Hz). ^{13}C{^{1}H} NMR (DMSO-d_6, 50.3 MHz): δ 28.5 (s, Me, CMe_2), 30.1 (s, *Me*CO), 30.8 (s, C$^{\beta}$H$_2$), 35.0 (s, Me, CMe_2), 45.0 (s, CH_2Ar), 53.4 (s, C$^{\alpha}$H), 57.4 (s, *C*Me$_2$), 126.2 (s, CH, C4), 127.6 (s, CH, C5), 129.6 (s, CH, C6), 133.1 (s, CH, C3), 135.3 (s, C2), 142.8 (s, C1), 204.9 (s, CO). The ^{13}C NMR resonance corresponding to CH_2Cl_2 was not observed.

Synthesis of [Pd$_2${*C,N*-CH(CO$_2$Et)CH$_2$C$_6$H$_4$(CH$_2$CH$_2$NH$_2$)-2}$_2$(μ-Br)$_2$] (1c). Ethyl acrylate (0.095 mL, 0.874 mmol) was added to a solution of complex [Pd$_2${*C,N*-C$_6$H$_4$CH$_2$CH$_2$NH$_2$-2}$_2$(μ-Br)$_2$] (**A**; 245 mg, 0.399 mmol) in CH_2Cl_2 (15 mL) and the mixture was stirred for 1.5 h. Formation of a small amount of palladium(0) was observed. The suspension was filtered through a plug of Celite, the filtrate was concentrated to ca. 2 mL, and Et_2O (30 mL) was added to precipitate a small amount of a brown impurity, which was removed by filtration. The filtrate was concentrated to ca. 5 mL, and *n*-pentane (20 mL) was added. The suspension was filtered, and the solid was washed with *n*-pentane (2 x 5 mL) and air-dried to give complex **1c** as an orange solid. Yield: 237 mg, 0.291 mmol, 73%. Mp: 105

°C dec. Anal. Calcd for $C_{26}H_{36}Br_2N_2O_4Pd_2$ (813.224): C, 38.40; H, 4.46; N, 3.44. Found: C, 38.68; H, 4.53; N, 3.63. IR (cm^{-1}): ν(NH) 3232 br; ν(CO) 1660 s. ^{1}H NMR (DMSO-d_6, 300.1 MHz): δ 1.21 (t, 3 H, Me, $^3J_{HH}$ = 7.2 Hz), 2.20 (dd, 1 H, C$^{\beta}$H$_2$, $^2J_{HH}$ = 13.8, $^3J_{HH}$ = 6.9 Hz), 2.66 (m, partially obscured by the CH_2Ar signal, 1 H, NH_2), 2.71 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 10.2 Hz), 2.99–3.26 (m, 4 H, 2 H of CH_2N + 1 H of C$^{\beta}$H$_2$ + 1 H of CH_2Ar), 3.68 (dd, 1 H, C$^{\alpha}$H, $^3J_{HH}$ = 11.7, $^3J_{HH}$ = 6.9 Hz), 4.04 (m, 2 H, CH_2O), 4.85 (d, 1 H, NH_2, $^2J_{HH}$ = 10.2 Hz), 7.09–7.12 (m, 1 H, H6), 7.20–7.30 (m, 3 H, H3 + H4 + H5). ^{13}C{^{1}H} NMR (DMSO-d_6, 75.45 MHz): δ 14.4 (s, Me), 32.2 (s, C$^{\beta}$H$_2$), 32.6 (s, CH_2Ar), 41.1 (s, C$^{\alpha}$H), 47.6 (s, CH_2N), 59.3 (s, CH_2O), 126.3 (s, CH, C4), 126.5 (s, CH, C5), 128.5 (s, CH, C6), 130.6 (s, CH, C3), 137.5 (s, C2), 141.4 (s, C1), 176.1 (s, CO).

Synthesis of [Pd$_2${*C,N*-CH(CO$_2$Et)CH$_2$C$_6$H$_4$(CH$_2$CMe$_2$NH$_2$)-2}$_2$(μ-Cl)$_2$] (1d). Ethyl acrylate (0.250 mL, 2.23 mmol) was added to a solution of complex [Pd$_2${*C,N*-C$_6$H$_4$CH$_2$CMe$_2$NH$_2$-2}$_2$(μ-Cl)$_2$] (**B**; 400 mg, 0.689 mmol) in CH_2Cl_2 (15 mL) and the resulting mixture was stirred for 3 h. Formation of a small amount of palladium(0) was observed. The mixture was filtered through a plug of Celite, and the filtrate was concentrated to dryness. The yellow residue was stirred with Et_2O (25 mL) for 10 min, and the suspension was filtered. The solid was washed with Et_2O (3 x 3 mL) and air-dried to give complex **1d** as a yellow solid. Yield: 432 mg, 0.553 mmol, 80%. Mp: 145 °C dec. Anal. Calcd for $C_{30}H_{44}Cl_2N_2O_4Pd_2$ (780.428): C, 46.17; H, 5.68; N, 3.59. Found: C, 46.15; H, 5.85; N, 3.54. IR (cm^{-1}): ν(NH) 3236 m, 3146 m; ν(CO) 1640 s. ^{1}H NMR (DMSO-d_6, 300.1 MHz): δ 1.16 (s, 3 H, Me, CMe_2), 1.23 (t, 3 H, *Me*CH_2, $^3J_{HH}$ = 6.9 Hz), 1.40 (s, 3 H, Me, CMe_2), 2.11 (dd, 1 H, C$^{\beta}$H$_2$, $^2J_{HH}$ = 13.5, $^3J_{HH}$ = 7.2 Hz), 2.50 (d, one-half of the doublet was partially obscured by the DMSO resonance, 1 H, CH_2Ar), 2.78 (d, 1 H, NH_2, $^2J_{HH}$ = 11.7 Hz), 3.08 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.1 Hz), 3.17 ("t", 1 H, C$^{\beta}$H$_2$, $^2J_{HH} \approx {}^3J_{HH} \approx$ 11.7 Hz), 3.66 (dd, 1 H, C$^{\alpha}$H,

$^{3}J_{HH}$ = 11.1, $^{3}J_{HH}$ = 7.2 Hz), 4.07 (m, 2 H, CH_2O), 4.63 (d, 1 H, NH_2, $^{2}J_{HH}$ = 11.4 Hz), 7.10 (dd, 1 H, H6, $^{3}J_{HH}$ = 7.5, $^{4}J_{HH}$ = 1.5 Hz), 7.15–7.29 (m, 3 H, H3 + H4 + H5). $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 75.45 MHz): δ 14.4 (s, *Me*CH_2), 27.8 (s, Me, CMe_2), 31.7 (s, $C^{\beta}H_2$), 33.9 (s, Me, CMe_2), 39.9 (s, $C^{\alpha}H$), 44.3 (s, CH_2Ar), 56.2 (s, *C*Me_2), 59.4 (s, CH_2O), 125.4 (s, CH, C4), 126.5 (s, CH, C5), 128.6 (s, CH, C6), 132.2 (s, CH, C3), 134.3 (s, C2), 142.2 (s, C1), 176.6 (s, CO).

Synthesis of [Pd$_2${*C,N*-CH(C_5H_8)CHC_6H_4($CH_2CMe_2NH_2$)-2}$_2$(μ-Cl)$_2$] (1e). 2-Norbornene (62 mg, 0.650 mmol) was added to a suspension of complex [Pd_2{*C,N*-$C_6H_4CH_2CMe_2NH_2$-2}$_2$(μ-Cl)$_2$] (**B**; 150 mg, 0.258 mmol) in CH_2Cl_2 (5 mL) and the resulting mixture was stirred for 1 h. A yellow solid precipitated, which was collected by filtration, washed with CH_2Cl_2 (5 mL) and Et_2O (10 mL) and air-dried to give complex **1e** as a yellow solid. Yield: 181 mg, 0.235 mmol, 91%. Dec pt: 175 °C. Anal. Calcd for $C_{34}H_{48}Cl_2N_2Pd_2$ (768.504): C, 53.14; H, 6.30; N, 3.65. Found: C, 52.73; H, 6.18; N, 3.59. IR (cm^{-1}): ν(NH) 3214 w. The insolubility of complex **1e** in all common solvents prevented us from measuring its NMR spectra.

Synthesis of [Pd{*C,N*-CH(COMe)$CH_2C_6H_4CH_2CH_2NH_2$-2}Cl(CN^{t}Bu)]·H_2O (2a·H_2O). ^{t}BuNC (0.058 mL, 0.513 mmol) was added to a solution of complex **1a** (180 mg, 0.239 mmol) in CH_2Cl_2 (15 mL), and the mixture was stirred for 15 min. The resulting yellow solution was concentrated to ca. 1 mL, and Et_2O (20 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give a first crop of complex **2a**·H_2O as a colorless solid (104 mg). The filtrate was concentrated to ca. 5 mL and cooled in an ice bath for 30 min. A precipitate slowly formed. The suspension was filtered, and the solid was washed with *n*-pentane (2 x 5 mL) and air-dried to give a second crop of complex **2a**·H_2O as a colorless solid (88 mg). Yield: 192 mg, 0.402 mmol, 84%. Dec pt: 156

°C. Anal. Calcd for $C_{17}H_{25}BrN_2OPd·H_2O$ (477.732): C, 42.74; H, 5.70; N, 5.86. Found: C, 42.76; H, 5.76; N, 5.50. IR (cm^{-1}): ν(OH) 3494 br, ν(NH) 3235 m; ν(CN) 2219 vs; ν(CO) 1590 br. ^{1}H NMR (400.91 MHz): δ 1.50 (s, 9 H, CMe_3), 1.69 (s, 2 H, H_2O), 2.14 (s, 3 H, MeCO), 2.34 (dd, 1 H, $C^{\beta}H_2$, $^2J_{HH}$ = 13.6, $^3J_{HH}$ = 6.4 Hz), 2.47 (br s, 1 H, NH_2), 2.76 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.4 Hz), 3.00 (br d, 1 H, NH_2, $^2J_{HH}$ = 9.2 Hz), 3.08–3.16 (m, 1 H, CH_2Ar), 3.29–3.35 (m, 2 H, CH_2N), 3.48 (dd, 1 H, $C^{\beta}H_2$, $^2J_{HH}$ = 13.6, $^3J_{HH}$ = 11.2 Hz), 4.18 (dd, 1 H, $C^{\alpha}H$, $^3J_{HH}$ = 10.4, $^3J_{HH}$ = 6.8 Hz), 7.08 (d, 1 H, H6, $^3J_{HH}$ = 7.2 Hz), 7.19–7.25 (m, 3 H, H3 + H4 + H5). ^{13}C{^{1}H} NMR (100.81 MHz): δ 29.5 (s, *Me*CO), 30.1 (s, C*Me*$_3$), 30.3 (s, $C^{\beta}H_2$), 32.8 (s, CH_2Ar), 42.0 (s, $C^{\alpha}H$), 47.5 (s, CH_2N), 58.3 (br s, *C*Me$_3$), 126.9 (s, CH, C4 + C5), 127.9 (t, CN, $^1J_{CN}$ = 20.3 Hz.), 128.5 (s, CH, C6), 130.7 (s, CH, C3), 136.6 (s, C2), 140.8 (s, C1), 203.8 (s, CO). Single crystals of **2a**·$CHCl_3$ suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-pentane into a solution of **2a**·H_2O in $CHCl_3$.

Synthesis of [Pd{*C,N*-CH(COMe)$CH_2C_6H_4$($CH_2CMe_2NH_2$)-2}Cl(NC_5H_4Me-4)] (2b-1). 4-Picoline (0.080 mL, 0.822 mmol) was added to a suspension of complex **1b**·1/4CH_2Cl_2 (250 mg, 0.337 mmol) in CH_2Cl_2 (10 mL), and the mixture was stirred for 20 min. The resulting solution was concentrated to ca. 2 mL, and Et_2O (15 mL) was added to precipitate a small amount of a yellow impurity, which was removed by filtration. The filtrate was concentrated to ca. 2 mL and *n*-pentane (30 mL) was added. A yellow suspension formed, which was stirred in an ice bath for 30 min, and then filtered. The solid was washed with *n*-pentane (2 x 5 mL) and air-dried to give complex **2b-1** as a pale yellow solid. Yield: 303 mg, 0.668 mmol, 99%. Dec pt: 144 °C. Anal. Calcd for $C_{20}H_{27}ClN_2OPd$ (453.314): C, 52.99; H, 6.00; N, 6.18. Found: C, 53.16; H, 6.34; N, 6.23. IR (cm^{-1}): ν(NH) 3231 w, 3120 w; ν(C=N) 1617 s; ν(CO) 1583 vs. ^{1}H NMR (400.91 MHz): δ 1.42 (s, 3 H, Me, CMe_2), 1.45 (s, 3 H, Me, CMe_2), 1.99 (dd, 1 H, $C^{\beta}H_2$, $^2J_{HH}$ = 12.3, $^3J_{HH}$ = 4.8 Hz), 2.06 (s, 3 H, MeCO), 2.35 (s,

3 H, Me, pic), 2.53 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.4 Hz), 2.57 (br d, 1 H, NH_2, $^2J_{HH}$ = 10.2 Hz), 3.04 (br d, 1 H, NH_2, $^2J_{HH}$ = 10.2 Hz), 3.20 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.4 Hz), 3.44–3.58 (m, 2 H, C$^{\alpha}$H + 1 H of C$^{\beta}H_2$), 7.09 ("d", 2 H, *m*-H, pic, $^3J_{HH}$ = 6.0 Hz), 7.19 (d, 1 H, H6, $^3J_{HH}$ = 7.2 Hz), 7.26–7.29 (m, 2 H, H3 + H4), 7.31–7.37 (m, 1 H, H5), 8.22 ("d", 2 H, *o*-H, pic, $^3J_{HH}$ = 6.0 Hz). $^{13}C\{^1H\}$ NMR (100.81 MHz): δ 21.0 (s, Me, pic), 28.1 (s, Me, CMe_2), 30.0 (s, *Me*CO), 31.2 (s, C$^{\beta}H_2$), 35.1 (s, Me, CMe_2), 44.9 (s, CH_2Ar), 46.2 (s, C$^{\alpha}$H), 56.5 (s, *C*Me_2), 125.9 (s, *m*-CH, pic), 126.0 (s, CH, C4), 126.7 (s, CH, C5), 128.3 (s, CH, C6), 133.4 (s, CH, C3), 134.9 (s, C2), 142.2 (s, C1), 149.7 (s, *p*-C, pic), 151.9 (s, *o*-CH, pic), 203.4 (s, CO). Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of a 1:1 mixture of Et_2O and *n*-pentane into a solution of **2b-1** in $CHCl_3$.

Synthesis of [Pd{*C,N*-CH(COMe)$CH_2C_6H_4(CH_2CMe_2NH_2)$-2}Cl(CNXy)] (2b-2). XyNC (92 mg, 0.701 mmol) was added to a suspension of complex **1b**·1/4CH_2Cl_2 (250 mg, 0.337 mmol) in CH_2Cl_2 (15 mL), the mixture was stirred for 15 min and filtered through a plug of Celite. The filtrate was concentrated to ca. 2 mL, and Et_2O (25 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give a first crop of complex **2b-2** as a pale yellow solid (256 mg). The filtrate was concentrated to ca. 3 mL, and *n*-pentane (20 mL) was added. The suspension was filtered, and the solid was washed with *n*-pentane (2 x 5 mL) and air-dried to give a second crop of complex **2b-2** as a pale yellow solid (65 mg). Yield: 321 mg, 0.653 mmol, 97%. Mp: 135 °C dec. Anal. Calcd for $C_{23}H_{29}ClN_2OPd$ (491.314): C, 56.22; H, 5.95 N, 5.70. Found: C, 55.90; H, 5.67; N, 5.63. IR (cm^{-1}): ν(NH) 3205 m; ν(C=N) 2189 vs, 2177 vs; ν(CO) 1625 vs. ^1H NMR (400.91 MHz): δ 1.37 (s, 3 H, Me, CMe_2), 1.50 (s, 3 H, Me, CMe_2), 2.27 (s, 3 H, MeCO), 2.29 (dd, partially obscured by the MeCO signal, 1 H, C$^{\beta}H_2$, $^2J_{HH}$ = 14.0, $^3J_{HH}$ = 7.2 Hz), 2.43 (s, 6 H, Me, Xy), 2.52 (dd, 1 H, CH_2Ar, $^2J_{HH}$ = 14.4, $^4J_{HH}$ = 1.6 Hz), 2.78 (br d, 1 H, NH_2, $^2J_{HH}$ = 11.0 Hz), 2.90

(br d, 1 H, NH_2, $^2J_{HH}$ = 11.0 Hz), 3.25 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.4 Hz), 3.56 (dd, 1 H, $C^{\beta}H_2$, $^2J_{HH}$ = 14.0, $^3J_{HH}$ = 11.2 Hz), 4.40 (dd, 1 H, $C^{\alpha}H$, $^3J_{HH}$ = 11.2, $^3J_{HH}$ = 7.2 Hz), 7.11–7.25 (m, 7 H, Ar + Xy). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 18.8 (s, Me, Xy), 28.1 (s, Me, CMe_2), 30.0 (s, *Me*CO), 30.2 (s, $C^{\beta}H_2$), 35.5 (s, Me, CMe_2), 40.2 (s, $C^{\alpha}H$), 44.8 (s, CH_2Ar), 57.2 (s, *C*Me_2), 125.9 (s, CH, C4), 127.2 (s, CH, C5), 128.1 (s, *m*-CH, Xy), 128.9 (s, CH, C6), 129.9 (s, *p*-CH, Xy), 132.7 (s, CH, C3), 134.0 (s, C2), 135.6 (s, *o*-C, Xy), 141.8 (s, C1), 204.7 (s, CO). The ^{13}C NMR resonances corresponding to the *i*-C of Xy and the CN group are not observed.

Synthesis of [Pd{*C,N*-CH(CO$_2$Et)CH$_2$C$_6$H$_4$(CH$_2$CMe$_2$NH$_2$)-2}Cl(NC$_5$H$_4$Me-4)] (2d-1). 4-Picoline (0.045 mL, 0.460 mmol) was added to a solution of complex **1d** (150 mg, 0.192 mmol) in CH_2Cl_2 (10 mL). The solution was stirred for 30 min and filtered through a plug of Celite. The filtrate was concentrated to ca. 1 mL and Et_2O (30 mL) was added. The resulting solution was cooled at 0 ºC in an ice bath. A yellow precipitate slowly formed. The suspension was filtered, and the solid was washed with Et_2O (2 x 3 mL) and air-dried to give a first crop of complex **2d-1** as a pale yellow solid (77 mg). The filtrate was concentrated to ca. 5 mL, and the resulting suspension was filtered. The solid was washed with Et_2O (5 mL) and air-dried to give a second crop of complex **2d-1** as a pale yellow solid (74 mg). Yield: 151 mg, 0.312 mmol, 81%. Mp: 127 °C. Anal. Calcd for $C_{21}H_{29}ClN_2O_2Pd$ (483.34): C, 52.18; H, 6.05; N, 5.80. Found: C, 51.91; H, 6.38; N, 5.47. IR (cm^{-1}): ν(NH) 3231 w, 3182 m, 3110 m; ν(CO) 1651 s; ν(C=N) 1617 m. ^1H NMR (300.1 MHz): δ 1.34 (t, 3 H, *Me*CH_2, $^3J_{HH}$ = 7.1 Hz), 1.46 (s, 3 H, Me, CMe_2), 1.47 (s, 3 H, Me, CMe_2), 2.08 (dd, 1 H, $C^{\beta}H_2$, $^2J_{HH}$ = 13.9, $^3J_{HH}$ = 7.1 Hz), 2.34 (s, 3 H, Me, pic), 2.56 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.6 Hz), 2.94 (dd, 1 H, $C^{\alpha}H$, $^3J_{HH}$ = 11.3, $^3J_{HH}$ = 7.1 Hz), 2.96 (br d, 1 H, NH_2, $^2J_{HH}$ = 11.0 Hz), 3.06 (br d, 1 H, NH_2, $^2J_{HH}$ = 11.0 Hz), 3.19 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.6 Hz), 3.26 (dd, 1 H, $C^{\beta}H_2$, $^2J_{HH}$ = 13.9, $^3J_{HH}$ = 11.5 Hz), 4.18 (m, 2 H, CH_2O), 6.95–6.98 (m, 1 H, H6), 7.04 (“d”, 2 H, *m*-H, pic, $^3J_{HH}$ = 6.6

Hz), 7.24–7.28 (m, 3 H, H3 + H4 + H5), 8.13 ("d", 2 H, *o*-H, pic, $^3J_{HH}$ = 6.6 Hz). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 14.5 (s, *Me*CH_2), 21.0 (s, Me, pic), 28.5 (s, Me, CMe_2), 30.7 (s, $C^{\alpha}H$), 32.8 (s, $C^{\beta}H_2$), 35.1 (s, Me, CMe_2), 44.9 (s, CH_2Ar), 56.3 (s, *C*Me_2), 60.0 (s, CH_2O), 125.7 (s, *m*-CH, pic), 125.8 (s, CH, C4), 126.7 (s, CH, C5), 128.2 (s, CH, C6), 133.1 (s, CH, C3), 134.6 (s, C2), 142.6 (s, C1), 149.3 (s, *p*-C, pic), 151.5 (s, *o*-CH, pic), 177.9 (s, CO).

Synthesis of [Pd{*C*,*N*-CH(CO_2Et)$CH_2C_6H_4$($CH_2CMe_2NH_2$)-2}Cl(NH_3)] (2d-2). NH_3 was bubbled for 10 min through a solution of complex **1d** (150 mg, 0.192 mmol) in CH_2Cl_2 (15 mL). The resulting mixture was stirred under a NH_3 atmosphere for 30 min and filtered through a plug of Celite. The filtrate was concentrated to ca. 2 mL, Et_2O (30 mL) was added, and the mixture was cooled at 0 ºC in an ice bath. A yellow precipitate slowly formed. The suspension was filtered, and the solid was washed with Et_2O (2 x 3 mL) and air-dried to give a first crop of complex **2d-2** as a pale yellow solid (102 mg). The filtrate was concentrated to ca. 5 mL, and *n*-pentane was added (20 mL). The suspension was filtered, and the solid was washed with *n*-pentane Et_2O (2 x 5 mL) and air-dried to give a second crop of complex **2d-2** (21 mg) as a pale yellow solid. Yield: 123 mg, 0.301 mmol, 78%. Dec pt: 122 °C. Anal. Calcd for $C_{15}H_{25}ClN_2O_2Pd$ (407.244): C, 44.24; H, 6.19; N, 6.88. Found: C, 43.96; H, 6.17; N, 6.67. IR (cm^{-1}): ν(NH) 3318 m, 3257 m, 3179 br; ν(CO) 1640 vs. ^1H NMR (300.1 MHz): δ 1.31 (t, 3 H, *Me*CH_2, $^3J_{HH}$ = 6.9 Hz), 1.34 (s, 3 H, Me, CMe_2), 1.45 (s, 3 H, Me, CMe_2), 1.79 (s, 3 H, NH_3), 2.07 (dd, 1 H, $C^{\beta}H_2$, $^2J_{HH}$ = 13.8, $^3J_{HH}$ = 5.8 Hz), 2.52 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.6 Hz), 2.66 (br s, partially obscured by the $C^{\alpha}H$ signal, 1 H, NH_2), 2.74 (dd, 1 H, $C^{\alpha}H$, $^3J_{HH}$ = 11.8, $^3J_{HH}$ = 5.8 Hz), 3.00–3.14 (m, 3 H, 1 H of CH_2Ar + 1 H of $C^{\beta}H_2$ + 1 H of NH_2), 4.16 (m, 2 H, CH_2O), 7.06–7.10 (m, 1 H, H6), 7.12–7.29 (m, 3 H, H3 + H4 + H5). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 14.5 (s, *Me*CH_2), 28.3 (s, Me, CMe_2), 30.0 (s, $C^{\alpha}H$), 32.6 (s, $C^{\beta}H_2$), 34.9 (s, Me, CMe_2), 45.2 (s, CH_2Ar), 56.2 (s, *C*Me_2), 60.1 (s, CH_2O), 125.8 (s, CH,

C4), 127.2 (s, CH, C5), 128.3 (s, CH, C6), 132.7 (s, CH, C3), 134.3 (s, C2), 142.1 (s, C1), 176.8 (s, CO).

Synthesis of [Pd{*C*,*N*-CH(CO$_2$Et)CH$_2$C$_6$H$_4$(CH$_2$CMe$_2$NH$_2$)-2}Cl(NHEt$_2$)]·1/3CH$_2$Cl$_2$ (2d-3·1/3CH$_2$Cl$_2$). NHEt$_2$ (0.034 mL, 0.327 mmol) was added to a solution of complex **1d** (120 mg, 0.153 mmol) in CH_2Cl_2 (15 mL). The solution was stirred for 30 min and filtered through a plug of Celite. The filtrate was concentrated to ca. 2 mL, Et_2O (30 mL) was added, and the mixture was cooled at 0 ºC in an ice bath. The suspension was filtered, and the solid was washed with Et_2O (2 x 3 mL) and air-dried to give a first crop of complex **2d-3**·1/3CH_2Cl_2 as a pale yellow solid (84 mg). The filtrate was concentrated to ca. 2 mL, and *n*-pentane (20 mL) was added. The suspension was filtered, and the solid was washed with *n*-pentane (2 x 5 mL) and air-dried to give a second crop of complex **2d-3**·1/3CH_2Cl_2 as a pale yellow solid (24 mg). Yield: 108 mg, 0.220 mmol, 72%. Dec pt: 126 °C. Anal. Calcd for $C_{19}H_{33}ClN_2O_2Pd$·1/3CH_2Cl_2 (491.649): C, 47.23; H, 6.90; N, 5.70. Found: C, 47.40; H, 6.91; N, 5.75. IR (cm^{-1}): ν(NH) 3251 m, 3219 m, 3146 w; ν(CO) 1633 vs. ^{1}H NMR (300.1 MHz): δ 0.82 (t, 3 H, Me, (*Me*CH$_2$)$_2$N, $^3J_{HH}$ = 7.2 Hz), 1.24 (t, 3 H, Me, (*Me*CH$_2$)$_2$N, $^3J_{HH}$ = 7.2 Hz), 1.31 (t, 3 H, *Me*CH$_2$O, $^3J_{HH}$ = 6.9 Hz), 1.42 (s, 3 H, Me, CMe$_2$), 1.44 (s, 3 H, Me, CMe$_2$), 2.12 (dd, 1 H, C$^{\beta}$H$_2$, $^2J_{HH}$ = 13.8, $^3J_{HH}$ = 6.6 Hz), 2.27–2.41 (m, 2 H, 1 H of (MeC*H*$_2$)$_2$N + 1 H of (MeC*H*$_2$)$_2$N), 2.44–2.55 (m, 2 H, 1 H of (MeC*H*$_2$)$_2$N + 1 H of CH$_2$Ar), 2.61 (dd, 1 H, C$^{\alpha}$H, $^3J_{HH}$ = 11.4, $^3J_{HH}$ = 6.6 Hz), 2.76–2.90 (m, 1 H, (MeC*H*$_2$)$_2$N), 3.01 (br d, 2 H, NH$_2$, $^3J_{HH}$ = 9.3 Hz), 3.12 (d, 1 H, CH$_2$Ar, $^2J_{HH}$ = 14.4 Hz), 3.17 (dd, 1 H, C$^{\beta}$H$_2$, $^2J_{HH}$ = 13.8, $^3J_{HH}$ = 11.7 Hz), 4.04 (m, 1 H, CH$_2$O), 4.24 (m, 1 H, CH$_2$O), 5.30 (s, CH_2Cl_2), 7.08–7.11 (m, 1 H, H6), 7.18–7.23 (m, 3 H, H3 + H4 + H5). The ^{1}H resonance attributable to N*H*Et$_2$ was obscured by the C$^{\beta}$H$_2$ and CH$_2$Ar signals. ^{13}C{^{1}H} NMR (75.45 MHz): δ 14.3 (s, *Me*CH$_2$O), 14.8 (s, Me, (MeCH$_2$)$_2$N), 15.2 (s, Me, (MeCH$_2$)$_2$N), 28.6 (s, Me,

CMe_2), 30.1 (s, $C^{\alpha}H$), 34.0 (s, $C^{\beta}H_2$), 35.2 (s, Me, CMe_2), 45.4 (s, CH_2Ar), 46.6 (s, CH_2, $(MeCH_2)_2N$), 48.1 (s, CH_2, $(MeCH_2)_2N$), 56.1 (s, CMe_2), 60.1 (s, CH_2O), 125.8 (s, CH, C4), 127.2 (s, CH, C5), 128.4 (s, CH, C6), 133.0 (s, CH, C3), 134.9 (s, C2), 142.2 (s, C1), 178.3 (s, CO). The ^{13}C NMR resonance corresponding to the CH_2Cl_2 was not observed. Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of Et_2O into a solution of **2d-3**·$1/3CH_2Cl_2$ in $CHCl_3$.

Synthesis of [Pd{*C*,*N*-CH(CO_2Et)$CH_2C_6H_4(CH_2CMe_2NH_2)$-2}Cl($CN^tBu$)] (2d-4). ^{t}BuNC (0.095 mL, 0.840 mmol) was added to a solution of complex **1d** (300 mg, 0.384 mmol) in CH_2Cl_2 (15 mL). The solution was stirred for 15 min and filtered through a plug of Celite. The filtrate was concentrated to ca. 2 mL and *n*-pentane (30 mL) was added. The suspension was filtered, and the solid was washed with *n*-pentane (2 x 5 mL) and air-dried to give complex **2d-4** as a pale yellow solid. Yield: 306 mg, 0.646 mmol, 84%. Dec pt: 150 °C. Anal. Calcd for $C_{24}H_{31}ClN_2O_2Pd$ (473.351): C, 50.75; H, 6.60; N, 5.92. Found: C, 50.64; H, 6.46; N, 6.16. IR (cm^{-1}): ν(NH) 3261 m, 3216 w; ν(CN) 2212 vs; ν(CO) 1643 vs. ^1H NMR (400.91 MHz): δ 1.28 (t, 3 H, *Me*CH_2, $^3J_{HH}$ = 7.2 Hz), 1.32 (s, 3 H, Me, CMe_2), 1.47 (s, 3 H, Me, CMe_2), 1.49 (s, 9 H, CMe_3), 2.38 (dd, 1 H, $C^{\beta}H_2$, $^2J_{HH}$ = 13.6, $^3J_{HH}$ = 6.8 Hz), 2.51 (dd, 1 H, CH_2Ar, $^2J_{HH}$ = 14.4, $^4J_{HH}$ = 1.2 Hz), 2.88 (br d, 1 H, NH_2, $^2J_{HH}$ = 11.2 Hz), 3.11 (br d, 1 H, NH_2, $^2J_{HH}$ = 11.2 Hz), 3.19 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.4 Hz), 3.36 (dd, 1 H, $C^{\beta}H_2$, $^2J_{HH}$ = 13.6, $^3J_{HH}$ = 11.6 Hz), 3.56 (dd, 1 H, $C^{\alpha}H$, $^3J_{HH}$ = 11.6, $^3J_{HH}$ = 6.8 Hz), 4.12 (m, 2 H, CH_2O), 7.07 (dd, 1 H, H6, $^3J_{HH}$ = 6.8, $^4J_{HH}$ = 1.6 Hz), 7.12 (dd, 1 H, H3, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 1.6 Hz), 7.17–7.24 (m, 2 H, H4 + H5). $^{13}C\{^1H\}$ NMR (100.81 MHz): δ 14.3 (s, *Me*CH_2), 26.6 (s, $C^{\alpha}H$), 28.2 (s, Me, CMe_2), 30.1 (s, CMe_3), 32.3 (s, $C^{\beta}H_2$), 35.4 (s, Me, CMe_2), 45.1 (s, CH_2Ar), 56.6 (s, CMe_2), 57.9 (s, CMe_3), 60.0 (s, CH_2O), 125.9 (s, CH, Ar), 127.1 (s, CH, Ar), 128.0 (br t, CN,

$^{1}J_{CN}$ = 19.5 Hz), 128.5 (s, CH, C6), 132.6 (s, CH, C3), 134.0 (s, C2), 141.9 (s, C1), 177.1 (s, CO).

Synthesis of [Pd{*C,N*-CH(CO$_2$Et)CH$_2$C$_6$H$_4$(CH$_2$CMe$_2$NH$_2$)-2}Cl(CNXy)] (2d-5). XyNC (110 mg, 0.838 mmol) was added to a solution of complex **1d** (300 mg, 0.384 mmol) in CH_2Cl_2 (15 mL). The solution was stirred for 15 min and filtered through a plug of Celite. The filtrate was concentrated to ca. 2 mL and Et_2O (25 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give complex **2d-5** as a pale yellow solid. Yield: 342 mg, 0.656 mmol, 85%. Mp: 169 °C dec. Anal. Calcd for $C_{24}H_{31}ClN_2O_2Pd$ (521.395): C, 55.29; H, 5.99; N, 5.37. Found: C, 55.28; H, 6.17; N, 5.13. IR (cm^{-1}): ν(NH) 3257 m, 3217 w; ν(CN) 2196 vs; ν(CO) 1646 vs. ^{1}H NMR (400.91 MHz): δ 1.25 (X part of an ABX$_3$ system, 3 H, *Me*CH$_2$, $^{3}J_{AX}$ = $^{3}J_{BX}$ = 7.2 Hz), 1.39 (s, 3 H, Me, CMe$_2$), 1.51 (s, 3 H, Me, CMe$_2$), 2.42 (s, 6 H, Me, Xy), 2.45 (dd, partially obscured by the signal of Me of Xy, 1 H, C$^{\beta}$H$_2$, $^{2}J_{HH}$ = 14.0, $^{3}J_{HH}$ = 7.2 Hz), 2.55 (d, 1 H, CH$_2$Ar, $^{2}J_{HH}$ = 14.4 Hz), 2.96 (br d, 1 H, NH$_2$, $^{2}J_{HH}$ = 11.2 Hz), 3.24 (d, 1 H, CH$_2$Ar, $^{2}J_{HH}$ = 14.4 Hz), 3.28 (br d, partially obscured by the CH$_2$Ar signal, 1 H, NH$_2$, $^{2}J_{HH}$ = 11.6 Hz), 3.35 (dd, 1 H, C$^{\beta}$H$_2$, $^{2}J_{HH}$ = 13.6, $^{3}J_{HH}$ = 12.0 Hz), 3.85 (dd, 1 H, C$^{\alpha}$H, $^{3}J_{HH}$ = 11.6, $^{3}J_{HH}$ = 7.2 Hz), 4.11, 4.18 (AB part of an ABX$_3$ system, 2 H, CH$_2$O, $^{2}J_{AB}$ = 10.4 Hz), 7.09–7.24 (m, 7 H, Ar + Xy). ^{13}C{^{1}H} NMR (100.81 MHz): δ 14.32 (s, *Me*CH$_2$), 18.6 (s, Me, Xy), 26.33 (s, C$^{\alpha}$H), 28.3 (s, Me, CMe$_2$), 32.3 (s, C$^{\beta}$H$_2$), 35.5 (s, Me, CMe$_2$), 45.1 (s, CH$_2$Ar), 56.87 (s, *C*Me$_2$), 60.3 (s, CH$_2$O), 126.0 (s, CH, C4), 127.2 (s, CH, C5), 127.9 (s, *m*-CH, Xy), 128.7 (s, CH, C6), 129.6 (s, *p*-CH, Xy), 132.7 (s, CH, C3), 133.9 (s, C2), 135.7 (s, *o*-C, Xy), 141.9 (s, C1), 177.2 (s, CO). The ^{13}C NMR resonances corresponding to the *i*-C of Xy and the CN group are not observed.

Synthesis of [Pd{*C,N*-CH(C$_5$H$_8$)CHC$_6$H$_4$CH$_2$CMe$_2$NH$_2$-2}Cl(NC$_5$H$_4$Me-4)]·1/2CH$_2$Cl$_2$ (2e-1·1/2CH$_2$Cl$_2$). 4-Picoline (0.060 mL, 0.616 mmol) was added to a

suspension of complex **1e** (120 mg, 0.156 mmol) in CH_2Cl_2 (10 mL), and the resulting yellow solution was stirred for 20 min. The mixture was filtered through a plug of Celite, the filtrate was concentrated to ca. 1 mL, and Et_2O (20 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give complex **2e-1**·1/2CH_2Cl_2 as a colorless solid. Yield: 143 mg, 0.275 mmol, 88%. Mp: 129 °C. Anal. Calcd for $C_{23}H_{31}ClN_2Pd$·1/2CH_2Cl_2 (519.845): C, 54.30; H, 6.20; N, 5.39. Found: C, 54.30; H, 6.42; N, 5.40. IR (cm^{-1}): ν(NH) 3271 m, 3189 m, 3125 m; ν(C=N) 1617. ^{1}H NMR (300.1 MHz): δ 0.63 (d, 1 H, C^bH_2, $^2J_{HH}$ = 9.5 Hz), 0.80 (d, 1 H, C^bH_2, $^2J_{HH}$ = 9.3 Hz), 1.22–1.26 (m, 2 H, C^dH_2), 1.32–1.63 (m, partially obscured by the CMe_2 signals, 2 H, C^eH_2), 1.49 (s, 3 H, Me, CMe_2), 1.53 (s, 3 H, Me, CMe_2), 1.80 (d, 1 H, NH_2, $^2J_{HH}$ = 10.4 Hz), 2.07 (d, 1 H, C^aH, $^3J_{HH}$ = 3.4 Hz), 2.22 (d, 1 H, $C^{\alpha}H$, $^3J_{HH}$ = 9.1 Hz), 2.30 (s, 3 H, Me, pic), 2.40 (d, 1 H, C^cH, $^3J_{HH}$ = 3.3 Hz), 2.62 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.4 Hz), 2.72 (d, 1 H, $C^{\beta}H$, $^3J_{HH}$ = 8.9 Hz), 2.88 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.4 Hz), 3.37 (d, 1 H, NH_2, $^2J_{HH}$ = 10.4 Hz), 5.30 (s, CH_2Cl_2), 6.96 ("d", 2 H, *m*-H, pic, $^3J_{HH}$ = 5.3 Hz), 7.20–7.30 (m, 4 H, H3 + H4 + H5 + H6), 8.04 (br s, 2 H, *o*-H, pic). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 20.9 (s, Me, pic), 28.2 (s, Me, CMe_2), 30.3 (s, C^dH_2), 31.2 (s, C^eH_2), 36.0 (s, C^bH_2), 36.1 (s, Me, CMe_2), 40.8 (s, C^cH), 43.5 (s, C^aH), 43.9 (s, CH_2Ar), 44.1 (s, $C^{\alpha}H$), 51.6 (s, $C^{\beta}H$), 55.3 (s, CH_2Cl_2), 124.4 (s, CH, C6), 124.9 (s, CH, C4), 125.3 (s, *m*-CH, pic), 125.9 (s, CH, C5), 133.1 (s, CH, C3), 136.1 (s, C2), 145.4 (s, C1), 148.4 (s, *p*-C pic), 151.6 (s, *o*-CH, pic). The ^{13}C NMR resonance attributable to *C*Me_2 was not observed.

Synthesis of [Pd{*C*,*N*-CH(C_5H_8)CHC_6H_4($CH_2CMe_2NH_2$)-2}Cl(PPh_3)] (2e-2). PPh_3 (70 mg, 0.266 mmol) was added to a suspension of complex **1e** (100 mg, 0.130 mmol) in CH_2Cl_2 (10 mL), and the resulting solution was stirred for 30 min. The mixture was filtered through a plug of Celite, the filtrate was concentrated to ca. 1 mL, and *n*-pentane (30 mL) was added. The suspension was filtered, and the solid was washed with *n*-pentane (2 x 5 mL) and

air-dried to give complex **2e-2** as a pale yellow solid. Yield: 124 mg, 0.192 mmol, 74%. Dec pt: 165 °C. Anal. Calcd for $C_{35}H_{39}ClNPPd$ (646.538): C, 65.02; H, 6.08; N, 2.17. Found: C, 65.00; H, 6.18; N, 2.15. IR (cm^{-1}): ν(NH) 3281, 3208, 3129. ^{1}H NMR (400.91 MHz, –60 ºC): δ 0.25 (br s, 2 H, C^bH_2), 1.11 (m, 2 H, 1 H of C^dH_2 + 1 H of C^eH_2), 1.22–1.31 (m, 1 H, C^eH_2), 1.42 (br s, 4 H, 1 Me of CMe_2 + 1 H of C^dH_2), 1.53 (s, 3 H, Me, CMe_2), 1.76 (br s, 1 H, $C^{\alpha}H$), 1.95 (br s, 1 H, NH_2), 2.01 (br s, 1 H, C^cH), 2.63–2.68 (m, 2 H, C^aH + 1 H of CH_2Ar), 2.82 (d, 1 H, $C^{\beta}H$, $^3J_{HH}$ = 8.4 Hz), 3.07 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.0 Hz), 3.90 (br s, 1 H, NH_2), 7.12 (d, 1 H, H6, $^3J_{HH}$ = 7.2 Hz), 7.28–7.67 (m, 18 H, H3 + H4 + H5 + PPh_3). $^{13}C\{^1H\}$ NMR (100.81 MHz, –60 ºC): δ 28.3 (s, Me, CMe_2), 30.1 (s, C^dH_2), 32.3 (d, C^eH_2, $^4J_{PC}$ = 4.7 Hz), 35.4 (s, C^bH_2), 35.9 (s, Me, CMe_2), 40.5 (s, C^cH), 44.6 (s, CH_2Ar), 46.7 (d, $C^{\alpha}H$, $^2J_{PC}$ = 9.5 Hz), 50.5 (d, C^aH, $^3J_{PC}$ = 5.1 Hz), 50.8 (s, $C^{\beta}H$), 55.3 (s, *C*Me_2), 124.3 (s, CH, C4), 125.4 (s, CH, C6), 126.9 (s, CH, Ar), 127.4 (d, *o*-CH, PPh_3, $^2J_{PC}$ = 10.4 Hz), 129.8 (s, *p*-CH, PPh_3), 132.70 (s, CH, Ar), 132.75 (d, *i*-C, PPh_3, $^1J_{PC}$ = 48.1 Hz) 134.9 (br s, *m*-CH, PPh_3), 135.1 (s, C2), 147.4 (s, C1). $^{31}P\{^1H\}$ NMR (121.50 MHz): δ 34.7 (s).

Synthesis of [Pd{*C,N*-CH(C_5H_8)CHC_6H_4($CH_2CMe_2NH_2$)-2}Cl(CN^tBu)]·1/2H_2O (2e-3·1/2H_2O). ^{t}BuNC (0.110 mL, 0.073 mmol) was added to a suspension of complex **1e** (350 mg, 0.455 mmol) in CH_2Cl_2 (15 mL), and the resulting solution was stirred for 15 min. The mixture was filtered through a plug of Celite, the filtrate was concentrated to ca. 1 mL and *n*-pentane (30 mL) was added. The suspension was filtered, and the solid was washed with *n*-pentane (2 x 5 mL) and air-dried to give complex **2e-3**·1/2H_2O as a pale yellow solid. Yield: 390 mg, 0.818 mmol, 90%. Mp: 157 ºC dec. Anal. Calcd for $C_{22}H_{33}ClN_2Pd$·1/2H_2O (476.398): C, 55.46; H, 7.19; N, 5.88. Found: C, 55.74; H, 7.18; N, 6.04. IR (cm^{-1}): ν(NH) 3194 m; ν(CN) 2191 vs. ^{1}H RMN (400.91 MHz): δ 1.18–1.31 (m, 2 H, 1 H of C^dH_2 + 1 H of C^eH_2), 1.37 (s, 3 H, Me, CMe_2), 1.41 (m, partially obscured by the CMe_3 signal, 1 H, C^bH_2),

1.44 (s, 9 H, CMe_3), 1.48 (s, 3 H, Me, CMe_2), 1.49–1.56 (m, 1 H, C^dH_2 or C^eH_2), 1.60 (s, 1 H, H_2O), 1.66–1.73 (m, 1 H, C^dH_2 or C^eH_2), 1.92 (br d, 1 H, NH_2, $^2J_{HH}$ = 11.2 Hz), 2.21 (m, 1 H, C^bH_2), 2.36 (d, 1 H, C^aH, $^4J_{HH}$ = 2.0 Hz), 2.47 (dd, 1 H, CαH, $^3J_{HH}$ = 8.8, $^4J_{HH}$ = 2.0 Hz), 2.56–2.59 (m, 2 H, 1 H of CH_2Ar + C^cH), 2.76 (d, 1 H, CβH, $^3J_{HH}$ = 8.4 Hz), 2.87 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.4 Hz), 3.27 (br d, 1 H, NH_2, $^2J_{HH}$ = 10.4 Hz), 7.10 (dd, 1 H, H3, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.6 Hz), 7.14 (td, 1 H, H4, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.6 Hz), 7.22 (td, 1 H, H5, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.6 Hz), 7.38 (br d, 1 H, $^3J_{HH}$ = 8 Hz). $^{13}C\{^1H\}$ NMR (100.81 MHz): δ 29.0 (s, Me, CMe_2), 29.9 (s, Me, CMe_3), 30.6 (s, C^dH_2), 31.6 (s, C^eH_2), 36.3 (s, Me, CMe_2), 37.1 (s, C^bH_2), 42.2 (s, C^cH), 44.0 (s, CH_2Ar), 47.8 (s, C^aH), 50.8 (s, CβH), 53.8 (s, CαH), 55.3 (s, *C*Me_2), 57.0 (s, *C*Me_3), 124.2 (s, CH, C6), 124.9 (s, CH, C4), 126.8 (s, CH, C5), 132.5 (s, CH, C3), 134.0 (br t, CN, $^1J_{CN}$ = 20.1 Hz), 134.8 (s, C2), 146.4 (s, C1).

Synthesis of [Pd{*C*,*N*-CH(C_5H_8)CHC_6H_4($CH_2CMe_2NH_2$)-2}Cl(CNXy)] (2e-4). XyNC (110 mg, 0.838 mmol) was added to a suspension of complex **1e** (300 mg, 0.390 mmol) in CH_2Cl_2 (15 mL), and the resulting solution was stirred for 15 min. The mixture was filtered through a plug of Celite, the filtrate was concentrated to ca. 1 mL and *n*-pentane (20 mL) was added. The suspension was filtered, and the solid was washed with *n*-pentane (2 x 5 mL) and air-dried to give complex **2e-4** as a pale yellow solid. Yield: 398 mg, 0.772 mmol, 99%. Dec pt: 162 °C. Anal. Calcd for $C_{26}H_{33}ClN_2Pd$ (515.434): C, 60.59; H, 6.45; N, 5.43. Found: C, 60.27; H, 6.72; N, 5.32. IR (cm^{-1}): ν(NH) 3274 w, 3196 m, 3129 w; ν(CN) 2166 vs. ^1H NMR (400.91 MHz): δ 1.27 (m, 2 H, 1 H of C^dH_2 + 1 H of C^eH_2), 1.39 (m, 1 H, C^bH_2), 1.44 (s, 3 H, Me, CMe_2), 1.52 (s, 3 H, Me, CMe_2), 1.54–1.71 (m, 2 H, 1 H of C^dH_2 + 1 H of C^eH_2), 1.99 (br d, 1 H, NH_2, $^2J_{HH}$ = 10.8 Hz), 2.30 (m, 1 H, C^bH_2), 2.36 (6 H, Me, Xy), 2.54 (d, 1 H, C^aH, $^4J_{HH}$ = 3.6 Hz), 2.57–2.63 (m, 3 H, 1 H of CH_2Ar + 1 C^cH + CαH), 2.83 (d, 1 H, CβH, $^3J_{HH}$ = 8.8 Hz), 2.93 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.4 Hz), 3.37 (br d, 1 H, NH_2, $^2J_{HH}$ = 10.8

Hz), 7.05 (d, 1 H, *m*-H, Xy, $^{3}J_{HH}$ = 7.6 Hz), 7.15–7.24 (m, 4 H, H3 + H4 + H5 + *p*-H, Xy), 7.40 (d, 1 H, $^{3}J_{HH}$ = 7.6 Hz). $^{13}C\{^{1}H\}$ NMR (75.45 MHz): δ 18.8 (s, Me, Xy), 28.1 (s, Me, CMe_2), 30.5 (s, $C^{d}H_2$), 31.6 (s, $C^{e}H_2$), 36.3 (s, Me, CMe_2), 37.3 (s, $C^{b}H_2$), 42.3 (s, $C^{c}H$), 43.9 (s, CH_2Ar), 48.2 (s, $C^{a}H$), 50.9 (s, $C^{\beta}H$), 55.61 (s, *C*Me_2), 55.63 (s, $C^{\alpha}H$), 124.3 (s, CH, C6), 124.9 (s, CH, C4), 126.9 (s, CH, C5), 127.8 (s, *m*-CH, Xy), 129.0 (s, *p*-CH, Xy), 132.5 (s, CH, C3), 134.7 (s, C2), 135.4 (s, *o*-C, Xy), 146.3 (s, C1). The ^{13}C NMR resonances corresponding to the *i*-C of Xy and the CN group are not observed. Single crystals of **2e-4**·1/2$CHCl_3$ suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-pentane into a solution of **2e-4** in $CHCl_3$.

Synthesis of [$PdBr_2${2-($NH_2CH_2CH_2$)C_6H_4CH=$CHCO_2Et$}$_2$] (3c). Method a. Ethyl acrylate (0.115 mL, 1.05 mmol) was added to a suspension of complex [Pd_2{*C,N*-$C_6H_4CH_2CH_2NH_2$-2}$_2$(μ-Br)$_2$] (**A**; 300 mg, 0.489 mmol) in $CHCl_3$ (15 mL) and the mixture was stirred for 48 h. Decomposition to metallic palladium was observed. The mixture was filtered through a plug of Celite, the filtrate was concentrated to ca. 2 mL, and Et_2O was added (30 mL). The suspension was filtered, and the yellow solid was washed with Et_2O (2 x 5 mL) and air-dried to give a first crop of crude complex **3c** as a yellow solid (209 mg). The filtrate was concentrated to ca. 5 mL, and a precipìtate formed. The suspension was filtered, and the solid was washed with *n*-pentane (2 x 5 mL) and air-dried to give a second crop of crude complex **4c** as a yellow solid (17 mg; total amount of crude **3c**: 226 mg, 0.321 mmol, 66%). **Method b**. A solution of complex **1c** (150 mg, 0.184 mmol) in CH_2Cl_2 (20 mL) was heated at 45 ºC for 12 h. Decomposition to metallic palladium was observed. The mixture was filtered through a plug of Celite, the filtrate was concentrated to ca. 1 mL, and Et_2O (20 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give crude complex **3c** as a yellow solid (77 mg, 1.109 mmol, 59%).

Recrystallization. Crude **3c** (200 mg, 0.283 mmol) was dissolved in acetone (15 mL), and the solution was filtered through a plug of Celite. The filtrate was concentrated to ca. 2 mL and cooled at 0 ºC in an ice bath. A yellow precipitate slowly formed. The suspension was filtered, and the solid was washed with cold acetone (3 mL) and Et_2O (10 mL) and air-dried to give pure complex **4c** as a yellow solid (47.5 mg, 0.067 mmol, 21%). Mp: 174 °C. Anal. Calcd for $C_{26}H_{34}Br_2N_2O_4Pd$ (704.787): C, 44.31; H, 4.86; N, 3.97. Found: C, 43.93; H, 4.85; N, 3.96. IR (cm^{-1}): ν(NH) 3290 m, 3229 m, 3143 m; ν(CO) 1706 vs. ^{1}H NMR (400.91 MHz): δ 1.33 (t, 3 H, Me, $^3J_{HH}$ = 7.2 Hz), 2.86 (br t, 2 H, NH_2, $^3J_{HH}$ = 6.0 Hz), 3.03 ("quint", 2 H, CH_2N, $^3J_{HH}$ = 6.4 Hz), 3.15 (t, 2 H, CH_2Ar, $^3J_{HH}$ = 6.8 Hz), 4.25 (q, 2 H, CH_2O, $^3J_{HH}$ = 7.2 Hz), 6.39 (d, 1 H, =C$^{\alpha}$H, $^3J_{HH}$ = 15.6 Hz), 7.25–7.35 (m, 3 H, H4 + H5 + H6), 7.57 (m, 1 H, H3), 8.06 (d, 1 H, =C$^{\beta}$H, $^3J_{HH}$ = 15.6 Hz). $^{13}C\{^1H\}$ NMR (100.81 MHz): δ 14.3 (s, Me), 34.9 (s, CH_2Ar), 46.6 (s, CH_2N), 60.6 (s, CH_2O), 120.8 (s, =C$^{\alpha}$H), 127.2 (s, CH, C3), 127.6 (s, CH, C4), 130.2 (s, CH, C5), 130.4 (s, CH, C6), 133.6 (s, C2), 136.7 (s, C1), 141.3 (s, =C$^{\beta}$H), 166.8 (s, CO).

Synthesis of [$PdCl_2${2-($NH_2CMe_2CH_2$)C_6H_4CH=CHCO_2Et}$_2$] (3d). A solution of complex **1d** (275 mg, 0.352 mmol) in $CHCl_3$ (15 mL) was heated at 60 ºC for 7 h. Decomposition to metallic palladium was observed. The solvent was removed, Et_2O (20 mL) was added to the residue, and the suspension was filtered through a plug of Celite. The filtrate was concentrated to ca. 1 mL, and *n*-hexane (20 mL) was added. The suspension was filtered, and the solid was washed with *n*-hexane (2 x 5 mL) and air-dried to give complex **3d** as a yellow solid. Yield: 155 mg, 0.231 mmol, 66%. Dec pt: 140 °C. Anal. Calcd for $C_{30}H_{42}Cl_2N_2O_4Pd$ (671.991): C, 53.62; H, 6.30; N, 4.17. Found: C, 53.21; H, 6.70; N, 4.36. IR (cm^{-1}): ν(NH) 3210 br; ν(CO) 1708 s. ^{1}H NMR (300.1 MHz): δ 1.34 (t, 3 H, *Me*CH_2, $^3J_{HH}$ = 7.1 Hz), 1.43 (s, 6 H, CMe_2), 2.94 (br s, 2 H, NH_2), 3.14 (s, 2 H, CH_2Ar), 4.26 (q, 2 H, CH_2O,

$^3J_{HH}$ = 7.1 Hz), 6.37 (d, 1 H, =C$^{\alpha}$H, $^3J_{HH}$ = 15.7 Hz), 7.26–7.37 (m, 3 H, H4 + H5 + H6), 7.60–7.62 (m, 1 H, H3), 8.02 (d, 1 H, =C$^{\beta}$H, $^3J_{HH}$ = 15.7 Hz). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 14.3 (s, *Me*CH_2), 29.7 (s, C*Me*$_2$), 45.5 (s, CH_2Ar), 57.4 (s, *C*Me_2), 60.6 (s, CH_2O), 120.1 (s, =C$^{\alpha}$H), 127.2 (s, CH, C3), 127.7 (s, CH, C4), 129.9 (s, CH, C5), 132.3 (s, CH, C6), 134.5 (s, C2), 136.1 (s, C1), 142.5 (s, =C$^{\beta}$H), 166.7 (s, CO). Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of Et_2O into a solution of **3d** in $ClCH_2CH_2Cl$.

Synthesis of [PdBr$_2${2-(NH$_2$CH$_2$CH$_2$)C$_6$H$_4$CH=CHPh}$_2$] (3f). Styrene (0.135 mL, 1.178 mmol) was added to a solution of complex [Pd$_2${*C,N*-C$_6$H$_4$CH$_2$CH$_2$NH$_2$-2}$_2$(μ-Br)$_2$] (**A**; 340 mg, 0.554 mmol) in CH_2Cl_2 (15 mL), and the mixture was stirred for 24 h. Decomposition to metallic palladium was observed. The mixture was filtered through a plug of Celite, the filtrate was concentrated to ca. 2 mL, and Et_2O (20 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give crude complex **3f** as a pale yellow solid (221 mg, 0.31 mmol, 56%). Crude **3f** (120 mg, 0.168 mmol) was dissolved in acetone (15 mL), and the solution was filtered through a plug of Celite. The filtrate was concentrated to ca. 2 mL and cooled at 0 ºC in an ice bath. A yellow precipitate slowly formed. The suspension was filtered, and the solid was washed with cold acetone (2 x 2 mL) and air-dried to give pure complex **3f** as a pale yellow solid (30 mg, 0.042 mmol, recrystallization yield: 25%). Mp: 185 °C. Anal. Calcd for $C_{32}H_{34}Br_2N_2Pd$ (712.854): C, 53.92; H, 4.81; N, 3.93. Found: C, 53.68; H, 4.82; N, 3.96. IR (cm^{-1}): ν(NH) 3308 m, 3252 m. ^{1}H NMR (400.91 MHz): δ 2.64 (br t, 2 H, NH_2, $^3J_{HH}$ = 5.6 Hz), 2.99–3.09 (m, 4 H, CH_2Ar + CH_2N), 6.99 (d, 1 H, =C$^{\alpha}$H, $^3J_{HH}$ = 16.0 Hz), 7.16 (dd, 1 H, H6, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 1.2 Hz), 7.21–7.28 (m, 3 H, H4 + H5 + *p*-H of Ph), 7.31 (d, partially obscured by the signal of *m*-H of Ph, 1 H, =C$^{\beta}$H, $^3J_{HH}$ = 15.2 Hz), 7.34 (t, 2 H, *m*-H, Ph, $^3J_{HH}$ = 7.7 Hz), 7.56 (d, 2 H, *o*-H, Ph,

$^{3}J_{HH}$ = 8.0 Hz), 7.59 (dd, 1 H, H3, $^{3}J_{HH}$ = 7.6, $^{4}J_{HH}$ = 1.2 Hz). $^{13}C\{^{1}H\}$ NMR (100.81 MHz): δ 35.3 (s, CH_2Ar), 46.3 (s, CH_2N), 125.5 (s, =C$^{\beta}$H), 126.5 (s, CH, C3), 126.9 (s, *o*-CH, Ph), 127.5 (s, CH, C4), 127.8 (s, CH, C5), 127.9 (s, *p*-CH, Ph), 128.7 (s, *m*-CH, Ph), 129.9 (s, CH, C6) 131.7 (s, =C$^{\alpha}$H), 134.6 (s, C1), 136.7 (s, C2), 137.2 (s, *i*-C, Ph).

Synthesis of [$PdCl_2${2-($NH_2CMe_2CH_2$)C_6H_4CH=CHPh}$_2$] (3g). Styrene (0.120 mL, 1.047 mmol) was added to a solution of complex [Pd_2{*C,N*-$C_6H_4CH_2CMe_2NH_2$-2}$_2$(μ-Cl)$_2$] (**B**; 150 mg, 0.258 mmol) in CH_2Cl_2 (10 mL), and the mixture was stirred for 48 h. Decomposition to metallic palladium was observed. The mixture was filtered through a plug of Celite, the filtrate was concentrated to ca. 1 mL, and Et_2O was added (20 mL). The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give a first crop of complex **3g** as a pale yellow solid (90 mg). The filtrate was concentrated to dryness, and the residue was stirred with Et_2O (10 ml). The suspension was filtered, and the solid was washed with Et_2O (5 mL) and air-dried to give a second crop of complex **3g** as a pale yellow solid (18 mg). Yield: 108 mg, 0.159 mmol, 62%. Mp: 177 °C dec. Anal. Calcd for $C_{36}H_{42}Cl_2N_2Pd$ (680.058): C, 63.58; H, 6.22; N, 4.12. Found: C, 63.38; H, 6.51; N, 4.48. IR (cm^{-1}): ν(NH) 3273 m, 3197 s, 3122 m. ^{1}H NMR (400.91 MHz): δ 1.42 (s, 6 H, CMe_2), 2.88 (br s, 2 H, NH_2), 3.15 (s, 2 H, CH_2Ar), 6.99 (d, 1 H, =C$^{\alpha}$H, $^{3}J_{HH}$ = 16.0 Hz), 7.15–7.36 (m, 6 H, H4 + H5 + H6 + *m*-H of Ph + *p*-H of Ph), 7.39 (d, 1 H, =C$^{\beta}$H, $^{3}J_{HH}$ = 15.8 Hz), 7.53 (d, 2 H, *o*-H, Ph, $^{3}J_{HH}$ = 7.2 Hz), 7.64 (d, 1 H, H3, $^{3}J_{HH}$ = 7.5 Hz). $^{13}C\{^{1}H\}$ NMR (100.81 MHz): δ 29.8 (s, C*Me*$_2$), 45.7 (s, CH_2Ar), 57.6 (s, *C*Me$_2$), 126.6 (s, CH, C3), 126.7 (s, *o*-CH, Ph), 126.8 (s, =C$^{\beta}$H), 127.4 (s, CH, C4), 127.5 (s, CH, C5), 127.8 (s, *p*-CH, Ph), 128.7 (s, *m*-CH, Ph), 131.1 (s, =C$^{\alpha}$H), 131.9 (s, CH, C6), 134.4 (s, C1), 137.3 (s, *i*-C, Ph), 137.5 (s, C2). Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of Et_2O into a solution of **3g** in CH_2Cl_2.

Synthesis of (*E*)-2-Styryl-phenethylamine (4f). 1,10-Phenanthroline monohydrate (21 mg, 0.105 mmol) was added to a solution of complex **3f** (75 mg, 0.105 mmol) in CH_2Cl_2 (10 mL) and the resulting mixture was stirred for 30 h. A yellow solid precipitated, which was separated by filtration and identified as [$PdBr_2$(phen)] by IR and ^{1}H NMR. The solvent was removed from the filtrate, *n*-pentane (30 mL) was added to the residue, and the resulting suspension was filtered through a plug of Celite. The solvent was removed from the filtrate under vacuum to give compound **4f** as a colorless liquid. Yield: 23 mg, 0.103 mmol, 49%. IR (cm^{-1}): ν(NH) 3370 w. ^{1}H NMR (400.91 MHz): δ 1.22 (br s, 2 H, NH_2), 2.93 (m, 4 H, CH_2Ar + CH_2N), 6.99 (d, 1 H, =C$^{\alpha}$H, $^3J_{HH}$ = 16.0 Hz), 7.12–7.28 (m, 4 H, H4 + H5 + H6 + *p*-H of Ph), 7.36 (t, 2 H, *m*-H, Ph, $^3J_{HH}$ = 7.6 Hz), 7.37 (d, 1 H, =C$^{\beta}$H, $^3J_{HH}$ = 16.0 Hz), 7.51 (m, 2 H, *o*-H, Ph), 7.61 (m, 1 H, H3). ^{13}C{^{1}H} NMR (100.81 MHz): δ 37.6 (s, CH_2Ar), 43.1 (s, CH_2N), 125.9 (s, CH, C3), 126.0 (s, =C$^{\beta}$H), 126.5 (s, *o*-CH, Ph), 126.6 (s, CH, Ar), 127.6 (s, CH, Ar), 127.7 (s, CH of Ar + *p*-CH of Ph), 128.6 (s, *m*-CH, Ph), 130.1 (s, CH, C6), 130.4 (s, =C$^{\alpha}$H), 136.3 (s, C2), 137.5 (s, C1). The ^{13}C NMR resonance corresponding to *i*-C of Ph was not observed. EI-HRMS: exact mass calcd for $C_{16}H_{17}N$ 223.1361; found 223.1360; Δ = 0.0001.

Synthesis of (*E*)-2-Styryl-phentermine (4g). 1,10-Phenanthroline monohydrate (44 mg, 0.220 mmol) was added to a solution of complex **3g** (150 mg, 0.220 mmol) in CH_2Cl_2 (10 mL) and the resulting mixture was stirred for 30 h. A yellow solid precipitated, which was separated by filtration and identified as [$PdCl_2$(phen)] by IR and ^{1}H NMR. The solvent was removed from the filtrate, *n*-pentane (20 mL) was added to the residue, and the resulting suspension was filtered through a plug of Celite. The solvent was removed from the filtrate under vacuum to give compound **4g** as a colorless liquid. Yield: 103 mg, 0.410 mmol, 94%. IR (cm^{-1}): ν(NH) 3357 br. ^{1}H NMR (400.91 MHz): δ 1.01 (s, 6 H, CMe_2), 1.19 (br s, 2 H, NH_2), 2.74 (s, 2 H, CH_2Ar), 6.86 (d, 1 H, =C$^{\alpha}$H, $^3J_{HH}$ = 16.4 Hz), 7.07–7.15 (m, 4 H, H4 + H5

+ H6 + *p*-H of Ph), 7.23 (t, 2 H, *m*-H, Ph, $^3J_{HH}$ = 7.2 Hz), 7.37 (d, 1 H, =C$^{\beta}$H, $^3J_{HH}$ = 16.0 Hz), 7.38 (d, 2 H, *o*-H, Ph, $^3J_{HH}$ = 8.4 Hz), 7.53 (d, 1 H, H3, $^3J_{HH}$ = 8 Hz). $^{13}C\{^1H\}$ NMR (100.81 MHz): δ 30.7 (s, C*Me*$_2$), 46.7 (s, CH_2Ar), 51.1 (s, *C*Me$_2$), 125.9 (s, CH, C3), 126.3 (s, *o*-CH, Ph), 126.6 (s, CH, C4), 126.9 (s, CH, C5), 127.4 (s, =C$^{\beta}$H + *p*-CH of Ph), 128.5 (s, *m*-CH, Ph), 129.8 (s, =C$^{\alpha}$H), 131.9 (s, CH, C6), 136.4 (s, C1), 137.1 (s, C2), 137.5 (s, *i*-C, Ph). EI-HRMS: exact mass calcd for $C_{18}H_{21}N$ 251.1674; found 251.1667; Δ = 0.0007.

Synthesis of 1-(Acetylmethyl)-3,3-dimethyl-1,2,3,4-tetrahydroisoquinolinium Chloride (5b-HCl) and 1-(Acetylmethyl)-3,3-dimethyl-1,2,3,4-tetrahydroisoquinoline (5b). TlOTf (148 mg, 0.418 mmol) was added to a suspension of complex **1b**·1/4CH_2Cl_2 (140 mg, 0.202 mmol) in acetone (15 mL), and the resulting suspension was stirred for 12 h. The solvent was removed, THF (15 mL) was added, and the mixture was refluxed for 8 h. Decomposition to metallic palladium was observed. The suspension was filtered through a plug of Celite, and the solvent was removed from the filtrate. CH_2Cl_2 (5 mL) was added, and the resulting suspension was filtered. CH_2Cl_2 (15 mL) and Na_2CO_3 (200 mg, 1.88 mmol) were added to the filtrate, and the suspension was stirred for 3 h and filtered. The solvent was removed from the filtrate, and Et_2O (15 mL) was added to the residue. HCl was bubbled through the solution for 5 min. The resulting suspension was filtered, and the solid was washed with Et_2O (5 mL) and air-dried to give a first crop of compound **5b-HCl** as a very hygroscopic white solid (39 mg). The filtrate was concentrated to ca. 3 mL, and *n*-pentane was added. The suspension was filtered, and the solid was washed with *n*-pentane (2 x 5 mL) to give a second crop of compound **5b-HCl** (6 mg). Yield: 45 mg, 0.177 mmol, 44%. ^1H NMR (400.91 MHz): δ 1.44 (s, 3 H, Me, CMe_2), 1.73 (s, 3 H, Me, CMe_2), 2.28 (s, 3 H, MeCO), 2.77 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 16.4 Hz), 3.33 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 16.8 Hz), 3.51 (dd, 1 H, CH_2CO, $^2J_{HH}$ = 18.8, $^3J_{HH}$ = 5.2 Hz), 3.82 (dd, 1 H, CH_2CO, $^2J_{HH}$ = 18.8, $^3J_{HH}$ = 4.4

Hz), 4.97 (m, 1 H, CH), 7.07 (m, 1 H, H8), 7.11 (m, 1 H, H5), 7.22–7.27 (m, 2 H, H6 + H7), 9.12 (br s, 1 H, NH_2), 10.26 (br s, 1 H, NH_2). $^{13}C\{^1H\}$ NMR (100.81 MHz): δ 21.9 (s, Me, CMe_2), 27.5 (s, Me, CMe_2), 30.8 (s, *Me*CO), 39.6 (s, CH_2Ar), 46.1 (s, *C*H_2CO), 49.2 (s, CH), 54.9 (s, *C*Me_2), 124.7 (s, CH, C8), 127.5 (s, CH, C7), 128.1 (s, CH, C6), 129.6 (s, CH, C5), 130.5 (s, C8a), 131.1 (s, C4a), 207.8 (s, CO).

Na_2CO_3 (200 mg, 1.88 mmol) was added to a solution of **5b-HCl** (49 mg, 0.193 mmol) in CH_2Cl_2 (20 mL), the mixture was stirred for 4 h and then filtered. The solvent was removed from the filtrate, and cold *n*-pentane (20 mL) was added. The suspension was filtered through a plug of Celite, and the solvent was removed from the filtrate under vacuum to give compound **5b** as a colorless liquid. Yield: 38 mg, 0.175 mmol, 91%. IR (cm^{-1}): ν(NH) 3330br; ν(CO) 1714 vs. ^1H NMR (400.91 MHz): δ 1.10 (s, 3 H, Me, CMe_2), 1.23 (s, 3 H, Me, CMe_2), 1.78 (br s, 1 H, NH), 2.18 (s, 3 H, MeCO), 2.50 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 16.0 Hz), 2.79 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 15.6 Hz), 2.86 (dd, 1 H, CH_2CO, $^2J_{HH}$ = 17.6, $^3J_{HH}$ = 9.2 Hz), 3.11 (dd, 1 H, CH_2CO, $^2J_{HH}$ = 17.6, $^3J_{HH}$ = 3.2 Hz), 4.51 ("br d", 1 H, CH, $^3J_{HH}$ = 8 Hz), 7.04–7.09 (m, 2 H, H5 + H8), 7.12– 7.16 (m, 2 H, H6 + H7). $^{13}C\{^1H\}$ NMR (100.81 MHz): δ 24.4 (s, Me, CMe_2), 30.7 (s, *Me*CO), 31.6 (s, Me, CMe_2), 42.4 (s, CH_2Ar), 48.8 (s, *C*Me_2), 48.9 (s, CH), 51.0 (s, *C*H_2CO), 124.6 (s, CH, C8), 125.8 (s, CH, C7), 126.2 (s, CH, C6), 129.7 (s, CH, C5), 135.3 (s, C4a), 136.6 (s, C8a), 208.5 (s, CO). EI-HRMS: exact mass calcd for $C_{14}H_{19}NO$ 217.1467; found 217.1470; Δ = 0.0003.

Synthesis of 1-(Ethoxycarbonylmethyl)-1,2,3,4-tetrahydroisoquinoline (5c). 1,10-Phenanthroline monohydrate (56 mg, 0.282 mmol) was added to a solution of complex **3c** (150 mg, 0.283 mmol) in CH_2Cl_2 (40 mL) and the resulting mixture was stirred for 30 h. A yellow solid precipitated, which was separated by filtration and identified as [$PdBr_2$(phen)] by IR and ^1H NMR. The solvent was removed from the filtrate, *n*-pentane (10 mL) was added to

the residue, and the resulting suspension was filtered through a plug of Celite. The solvent was removed from the filtrate under vacuum to give compound **5c** as a colorless liquid. Yield: 82 mg, 0.237 mmol, 66%. IR (cm^{-1}): ν(NH) 3352 w; ν(CO) 1732 vs. ^{1}H NMR (300.10 MHz): δ 1.26 (t, 3 H, Me, $^3J_{HH}$ = 6.9 Hz), 2.15 (br s, 1 H, NH), 2.69–3.05 (m, 5 H, 2 H of CH_2CO + 2 H of CH_2Ar + 1 H of CH_2N), 3.20 (m, 1 H, CH_2N), 4.18 (q, 2 H, CH_2O, $^3J_{HH}$ = 6.9 Hz), 4.46 (dd, 1 H, CH, $^3J_{HH}$ = 9.6, $^3J_{HH}$ = 3.3 Hz), 7.07–7.17 (m, 4 H, C_6H_4). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 14.1 (s, Me), 29.7 (s, CH_2Ar), 40.6 (s, *C*H_2CO), 41.3 (s, CH_2N), 52.6 (s, CH), 60.5 (s, CH_2O), 125.8 (s, CH, C7 + C8), 126.2 (s, CH, C6), 129.4 (s, CH, C5), 135.4 (s, C4a), 137.5 (s, C8a), 172.3 (s, CO). FAB^+-MS: *m/z* 220.0 [$(M+1)^+$]. EI-HRMS: exact mass calcd for $C_{13}H_{17}NO_2$ 219.1259; found 219.1265; Δ = 0.0006.

Synthesis of 1-(Ethoxycarbonylmethyl)-3,3-dimethyl-1,2,3,4-tetrahydroisoquinoline (5d) and 1-(Ethoxycarbonylmethyl)-3,3-dimethyl-1,2,3,4-tetrahydroisoquinolinium Triflate (5d-HOTf). 1,10-Phenanthroline monohydrate (32 mg, 0.177 mmol) was added to a solution of complex **3d** (121 mg, 0.180 mmol) in CH_2Cl_2 (15 mL) and the resulting mixture was stirred for 30 h. A yellow solid precipitated, which was separated by filtration and identified as [$PdCl_2$(phen)] by IR and ^{1}H NMR. The solvent was removed from the filtrate, *n*-pentane (20 mL) was added to the residue, and the resulting suspension was filtered through a plug of Celite. The solvent was removed from the filtrate under vacuum to give compound **5d** as a colorless liquid. Yield: 60 mg, 0.242 mmol, 67%. IR (cm^{-1}): ν(NH) 3352 w; ν(CO) 1732 vs. ^{1}H NMR (300.1 MHz): δ 1.10 (s, 3 H, Me, CMe_2), 1.21 (t, 3 H, *Me*CH_2, $^3J_{HH}$ = 7.2 Hz), 1.26 (s, 3 H, Me, CMe_2), 2.53 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 15.9 Hz), 2.74 (dd, 1 H, CH_2CO, $^2J_{HH}$ = 16.5, $^3J_{HH}$ = 8.7 Hz), 2.80 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 15.9 Hz), 3.02 (dd, 1 H, CH_2CO, $^2J_{HH}$ = 16.5, $^3J_{HH}$ = 3.3 Hz), 3.20 (br s, 1 H, NH), 4.13 (q, 2 H, CH_2O, $^3J_{HH}$ = 7.2 Hz), 4.46 (br d, 1 H, CH, $^3J_{HH}$ = 8.7 Hz), 7.03–7.06 (m, 1 H, H5), 7.10–

7.17 (m, 3 H, H6 + H7 + H8). $^{13}C\{^{1}H\}$ NMR (75.45 MHz): δ 14.0 (s, *Me*CH_2), 24.3 (s, Me, CMe_2), 31.4 (s, Me, CMe_2), 41.1 (s, *C*H_2CO), 42.2 (s, CH_2Ar), 48.9 (s, *C*Me_2), 49.2 (s, CH), 60.4 (s, CH_2O), 124.7 (s, CH, C8), 125.8 (s, CH, C7), 126.2 (s, CH, C6), 129.5 (s, CH, C5), 135.1 (s, C4a), 135.9 (s, C8a), 172.4 (s, CO). FAB^+-MS: *m/z* 247.9 [$(M+1)^+$].

HOTf (0.050 mL, 0.565 mmol) was added to a solution of compound **5d** (35 mg, 1.141 mmol) in Et_2O (15 mL). The resulting mixture was stirred at 0 ºC in an ice bath for 30 min. The suspension was filtered, and the solid was washed with Et_2O (5 mL) and air-dried to give compound **5d-HOTf** as a colorless solid. Yield: 44 mg, 0.110 mmol, 78%. Mp: 89 ºC. Anal. Calcd for $C_{16}H_{22}F_3NO_5S$ (397.410): C, 48.36; H, 5.58; N, 3.52; S, 8.07. Found: C, 48.22; H, 5.63; N, 3.64; S, 8.10. IR (cm^{-1}): ν(NH) 3172 w; ν(CO) 1726 s. ^1H NMR (300.1 MHz): δ 1.16 (t, 3 H, *Me*CH_2, $^3J_{HH}$ = 7.2 Hz), 1.41 (s, 3 H, Me, CMe_2), 1.68 (s, 3 H, Me, CMe_2), 2.80 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 17.1 Hz), 3.21 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 17.1 Hz), 3.35 (m, 2 H, CH_2CO), 4.10 (m, 2 H, CH_2O), 4.90 (m, 1 H, CH), 7.14–7.21 (m, 2 H, H5 + H8), 7.28–7.34 (m, 2 H, H6 + H7), 7.88 (br s, 1 H, NH_2), 9.01 (br s, 1 H, NH_2). $^{13}C\{^{1}H\}$ NMR (75.45 MHz): δ 13.7 (s, *Me*CH_2), 21.0 (s, Me, CMe_2), 28.0 (s, Me, CMe_2), 35.7 (s, *C*H_2CO), 39.4 (s, CH_2Ar), 50.9 (s, CH), 55.9 (s, *C*Me_2), 62.2 (s, CH_2O), 120.1 (q, CF_3, $^1J_{CF}$ = 318.9 Hz), 124.9 (s, CH, C8), 127.9 (s, CH, C7), 128.7 (s, CH, C6), 128.7 (s, C8a), 129.7 (s, CH, C5), 131.0 (s, C4a), 172.3 (s, CO).

Synthesis of [Pd{*C,N*-$C_6H_4CH_2CMe_2NH_2$-2}Cl(PPh_3)] (6). PPh_3 (104 mg, 0.396 mmol) was added to a solution of complex [Pd_2{*C,N*-$C_6H_4CH_2CMe_2NH_2$-2}$_2$(μ-Cl)$_2$] (**B**; 115 mg, 0.198 mmol) in CH_2Cl_2 (10 mL), and resulting solution was stirred for 30 min. The mixture was filtered through a plug of $MgSO_4$, the filtrate was concentrated to ca. 3 mL, and Et_2O (15 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 3 mL) and air-dried to give complex **6** as a colorless solid. Yield: 148 mg, 0.268 mmol,

68%. Dec pt: 220 °C. Anal. Calcd for $C_{28}H_{29}ClNPPd$ (552.374): C, 60.88; H, 5.29; N, 2.53. Found: C, 60.55; H, 5.47; N, 2.57. IR (cm^{-1}): ν(NH) 3324 w, 3262 w. ^{1}H NMR (400.91 MHz): δ 1.34 (s, 6 H, Me), 3.01 (br s, 2 H, NH_2), 3.09 (s, 2 H, CH_2), 6.35 (td, 1 H, H5, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.2 Hz), 6.46 (ddd, 1 H, H6, $^3J_{HH}$ = 7.6, $^4J_{HP}$ = 4.5, $^4J_{HH}$ = 0.9 Hz), 6.74 (td, 1 H, H4, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 0.9 Hz), 6.80 (dd, 1 H, H3, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1.2 Hz), 7.26–7.31 (m, 6 H, *m*-H, PPh_3), 7.35–7.39 (m, 3 H, *p*-H, PPh_3), 7.52–7.57 (m, 6 H, *o*-H, PPh_3). $^{13}C\{^1H\}$ NMR (100.81): δ 30.0 (d, Me, $^4J_{CP}$ = 1.7 Hz), 49.6 (d, *C*Me_2, $^3J_{CP}$ = 2.2 Hz), 56.1 (s, CH_2), 123.3 (s, CH, C4), 125.1 (d, CH, C5, $^4J_{CP}$ = 3.9 Hz), 127.6 (s, CH, C3), 128.0 (d, *m*-CH, PPh_3, $^3J_{CP}$ = 10.5 Hz), 130.2 (d, *p*-CH, PPh_3, $^4J_{CP}$ = 2.3 Hz), 131.1 (d, *i*-C, PPh_3, $^1J_{CP}$ = 49.5 Hz), 134.7 (d, *o*-CH, PPh_3, $^3J_{CP}$ = 11.6 Hz), 136.5 (d, CH, C6, $^3J_{CP}$ = 9.8 Hz), 138.8 (s, C2), 153.1 (s, C1, C–Pd). $^{31}P\{^1H\}$ NMR (121.5 MHz): δ 34.5 (s). Single crystals suitable for an X-ray diffraction study, were obtained by slow diffusion of *n*-pentane into a solution of **6** in $CHCl_3$.

Synthesis of (*Z*)-2,2-Dimethyl-5-(ethoxycarbonyl)-4-(2,6-dimethylphenylimino)-1,2,3,4,5,6-hexahydro-3-benzo[*d*]azocine (7d). Method A: TlOTf (138 mg, 0.390 mmol) was added to a solution of complex **2d-5** (200 mg, 0.383 mmol) in acetone (30 mL), and the mixture was stirred for 5 min. The solvent was removed, toluene (20 mL) was added, and the resulting suspension was refluxed for 12 h. Decomposition to metallic palladium was observed. The solvent was removed, and CH_2Cl_2 (20 mL) was added. The suspension was filtered through a plug of Celite, and the filtrate was stirred with Na_2CO_3 (200 mg, 1.88 mmol) for 3 h. The suspension was filtered, and the solvent was removed from the filtrate. The ^{1}H MNR spectrum of this residue corresponds to a 1:3 mixture of compounds **5d** and **7d**. Et_2O (15 mL) was added to the residue, and the suspension was filtered through a plug of Celite. The filtrate was concentrated to ca. 2 mL and *n*-pentane (20 mL) was added, and the mixture cooled at 0 ºC in an ice bath. During this time, a colorless solid formed. The

suspension was filtered, and the solid was washed with *n*-pentane (2 x 2 mL) and air-dried to give a first crop of compound **7d** as a colorless solid (40 mg). The solvent was removed from the filtrate, and the residue was stirred in *n*-pentane (15 mL) at 0 ºC. The suspension was filtered, and the solid was whased with *n*-pentane (2 mL) to give a second crop of **7d** as a colorless solid (15 mg). Yield: 55 mg, 0.145 mmol, 38 %. The solvent was removed from the filtrate to get a colorless liquid, which proved to be the tetrahydroisoquinoline **5d** by ^{1}H NMR. **Method B:** A solution of complex **8d** (200 mg, 0.261 mmol) in $CHCl_3$ (15 mL) was heated at 70 ºC in a Carius tube for 24 h. Decomposition to metallic palladium was observed. The suspension was filtered through a plug of Celite, Na_2CO_3 (300 mg, 2.83 mmol) was added to the filtrate, and the mixture was stirred for 3 h. The suspension was filtered, the solvent was removed from the filtrate. The residue was dissolved in Et_2O (30 mL), and the solution was filtered through a plug of Celite. The filtrate was concentrated to ca. 4 mL, *n*-pentane (20 mL) was added, and the mixture was cooled at 0 ºC in an ice bath. The suspension was filtered, and the solid was washed with *n*-pentane (2 x 2 mL) and air-dried to afford compound **7d** as a colorless solid. Yield: 58 mg, 0.153 mmol, 59%. Mp: 178 °C. IR (cm^{-1}): ν(NH) 3385 w; ν(CO) 1744 vs; ν(C=N) 1634 vs. ^{1}H NMR (400.91 MHz): δ 1.05 (s, 3 H, Me, CMe_2), 1.23 (s, 3 H, Me, Xy), 1.34 (X part of an ABX_3 system, 3 H, *Me*CH_2, $^{3}J_{AX}$ = $^{3}J_{BX}$ = 7.2 Hz), 1.53 (s, 3 H, Me, CMe_2), 2.02 (s, 3 H, Me, Xy), 2.64 (d, 1 H, CH_2Ar, $^{2}J_{HH}$ = 14.4 Hz), 3.37 (d, partially obscured by the C*H*$_2$CH signal, 1 H, CH_2Ar), 3.39 (dd, partially obscured by the CH_2Ar signal, 1 H, C*H*$_2$CH, $^{2}J_{HH}$ = 15.2 Hz), 3.65 (br s, 1 H, NH), 3.72 (dd, 1 H, C*H*$_2$CH, $^{2}J_{HH}$ = 15.6, $^{3}J_{HH}$ = 11.2 Hz), 4.24, 4.37 (AB part of an ABX_3, 2 H, CH_2O, $^{2}J_{AB}$ = 10.7 Hz), 4.38 (dd, partially obscured by the CH_2O signal, 1 H, CH, $^{3}J_{HH}$ = 11.2, $^{3}J_{HH}$ = 8.4 Hz), 6.70–6.75 (m, 2 H, *m*-H + *p*-H, Xy), 6.90 (m, 1 H, *m*-H, Xy), 6.98–7.03 (m, 1 H, H10), 7.17 (m, 2 H, H8 + H9), 7.34 (m, 1 H, H7). ^{13}C{^{1}H} NMR (100.81 MHz): δ 14.2 (s, *Me*CH_2),

16.9 (s, Me, Xy), 17.6 (s, Me, Xy), 30.5 (s, Me, CMe_2), 30.8 (s, CMe_2), 35.3 (s, CH_2CH), 46.0 (s, CH_2Ar), 47.6 (s, CH), 53.4 (s, CMe_2), 61.2 (s, CH_2O), 122.4 (s, *p*-CH, Xy), 126.4 (s, CH, C9), 127.0 (s, CH, C8), 127.8 (s, *m*-CH, Xy), 127.9 (s, *m*-CH, Xy), 128.9 (s, *o*-C, Xy), 129.1 (s, *o*-C, Xy), 130.8 (s, CH, C10), 132.0 (s, CH, C7), 135.8 (s, C10a), 138.0 (s, C6a), 144.9 (br s, *i*-C, Xy), 153.3 (s, C=N), 170.7 (s, CO). ESI-HRMS: exact mass calcd for $C_{24}H_{31}N_2O_2$ 379.2386 [$(M+1)^+$]; found 379.2384 [$(M+1)^+$]; $\Delta = 0.0002$.

Synthesis of (*Z*)-2,2-Dimethyl-5,6-(2,3-norbornadiyl)-4-(2,6-dimethylphenylimino)-1,2,3,4,5,6-hexahydro-3-benzo[*d*]azocinium Triflate (7e-HOTf). TlOTf (103 mg, 0.291 mmol) was added to a solution of complex **2e-4** (150 mg, 0.291 mmol) in acetone (15 mL), the resulting suspension was stirred for 10 min, and solvent was removed. Toluene (15 mL) was added, and the mixture was heated at 80 ºC for 4 h. Decomposition to metallic palladium was observed. The toluene was removed, CH_2Cl_2 (15 mL) was added, and the resulting solution was filtered through a plug of Celite. The filtrate was concentrated to ca. 1 mL and Et_2O (20 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give compound **7e-HOTf** as a colorless solid. Yield: 106 mg, 0.203 mmol, 70%. An analytically pure sample of compound **7e-HOTf** was obtained by recrystallization from $CHCl_3/Et_2O$. Mp: 282 °C. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 137 (5.28×10^{-4} M). Anal. Calcd for $C_{27}H_{33}F_3N_2O_3S$ (522.632): C, 62.05; H, 6.36; N, 5.36, S, 6.13. Found: C, 61.63; H, 6.42; N, 5.53; S, 5.85. IR (cm^{-1}): ν(NH) 337 s, 3181 br; ν(C=N) = 1613 vs. ^{1}H NMR (acetone-d_6, 400.91 MHz): δ 1.22 (s, 3 H, Me, Xy), 1.31 (s, 3 H, Me, CMe_2), 1.66–1.71 (m, 1 H, CH_2), 1.74 (s, 3 H, Me, CMe_2), 1.82–1.94 (m, 3 H, CH_2), 2.16 (br d, 1 H, C^bH_2, $^2J_{HH}$ = 10.8 Hz), 2.87 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.8 Hz), 2.54 (br s, 1 H, C^cH), 3.21 (d, 1 H, C^aH, $^4J_{HH}$ = 3.6 Hz), 2.82 (d, 1 H, CH_2Ar, $^2J_{HH}$ = 14.4 Hz), 3.21 (s, 2 H, H5 + H6), 6.01 (br s, 1 H, NH), 7.02 (d, 1 H, *m*-H, Xy, $^3J_{HH}$ = 7.2 Hz), 7.16 (d, 1 H, *m*-H, Xy, $^3J_{HH}$ = 7.2 Hz), 7.21 (t, 1

H, *p*-H, Xy, $^{3}J_{HH}$ = 7.6 Hz), 7.30–7.32 (m, 2 H, H9 + H10), 7.33–7.39 (m, 1 H, H8), 7.56 (d, 1 H, H7, $^{3}J_{HH}$ = 7.6 Hz), 9.42 (br s, 1 H, NH). $^{13}C\{^{1}H\}$ NMR (acetone-d_6, 100.81 MHz): δ 16.5 (s, Me, Xy), 17.7 (s, Me, Xy), 28.2 (s, Me, CMe_2), 28.8 (s, $C^{d}H_2$), 30.2 (s, $C^{e}H_2$), 30.3 (s, Me, CMe_2), 39.1 (s, $C^{b}H_2$), 39.6 (s, $C^{c}H$), 41.3 (s, $C^{a}H$), 42.9 (s, CH_2Ar), 51.1 (s, CH, C5), 51.6 (s, CH, C6), 58.5 (s, *C*Me_2), 126.1 (s, CH, C7), 127.8 (s, CH, C9), 128.5 (s, CH, C8), 129.7 (s, *m*-CH, Xy), 130.0 (s, *m*-CH, Xy), 130.8 (s, *p*-CH, Xy), 131.1 (s, CH, C10), 136.2 (s, *o*-C, Xy), 137.1 (s, *o*-C, Xy), 137.2 (s, C10a), 140.2 (s, C6a), 167.6 (s, C4). The ^{13}C NMR resonances corresponding to the *i*-C of Xy is not observed. Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-pentane into a solution of **7e-HOTf** in acetone.

Synthesis of [Pd{*C*,*N*-CH(CO$_2$Et)CH$_2$C$_6$H$_4$(CH$_2$CMe$_2$NH$_2$)-2}(CNXy)$_2$]OTf (8d). XyNC (50 mg, 0.381 mmol) and TlOTf (102 mg, 0.289 mmol) were added to a suspension of complex **2d-5** (150 mg, 0.287 mmol) in acetone (15 mL). The resulting mixture was stirred for 2 h and then filtered through a plug of Celite. The solvent was removed from the filtrate, the residue was dissolved in CH_2Cl_2 (2 mL), and Et_2O (20 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to give complex **8d** as an orange solid. Yield: 195 mg, 0.254 mmol, 89%. Mp: 220 °C dec. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 142 (5.27 x 10^{-4} M). Anal. Calcd for $C_{34}H_{40}F_3N_3O_5PdS$ (766.190): C, 53.30; H, 5.26; N, 5.48; S, 4.18. Found: C, 53.11; H, 5.41; N, 5.73; S, 3.92. IR (cm^{-1}): ν(NH) 3217 m, 3128 m; ν(CN) 2200 vs, 2184 vs; ν(CO) 1678 vs. ^{1}H NMR (400.91 MHz): δ 1.28 (X part of an ABX_3 system, 3 H, *Me*CH_2, $^{3}J_{AX} = {}^{3}J_{BX}$ = 7.2 Hz), 1.38 (s, 3 H, Me, CMe_2), 1.70 (s, 3 H, Me, CMe_2), 2.31 (s, 6 H, Me, Xy), 2.42 (s, 6 H, Me, Xy), 2.55 (br d, 1 H, CH_2Ar, $^{2}J_{HH}$ = 14.4 Hz), 2.67 (dd, 1 H, $C^{\beta}H_2$, $^{2}J_{HH}$ = 13.6, $^{3}J_{HH}$ = 8.0 Hz), 3.28 (d, 1 H, CH_2Ar, $^{2}J_{HH}$ = 15.2 Hz), 3.54 (dd, 1 H, $C^{\beta}H_2$, $^{2}J_{HH}$ = 13.6, $^{3}J_{HH}$ = 11.2 Hz), 3.62 (br d, 1 H, NH_2, $^{2}J_{HH}$ = 10.8 Hz), 3.97 (br dd, 1 H,

$C^{\alpha}H$, $^{3}J_{HH}$ = 10.4, $^{3}J_{HH}$ = 8.4 Hz), 4.19 (AB part of an ABX_3 system, 2 H, CH_2O, $^{2}J_{AB}$ = 8.4 Hz), 5.35 (br d, 1 H, NH_2, $^{2}J_{HH}$ = 10.4 Hz), 7.04 (d, 2 H, *m*-H, Xy, $^{3}J_{HH}$ = 7.6 Hz), 7.15–7.26 (m, 7 H, 4 H of Ar + *m*-H and *p*-H of Xy), 7.33 (d, 1 H, *p*-H, Xy,$^{3}J_{HH}$ = 7.6 Hz). $^{13}C\{^{1}H\}$ RMN (100.81 MHz): δ 14.3 (s, *Me*CH_2), 18.6 (s, Me, Xy), 18.7 (s, Me, Xy), 27.5 (s, Me, CMe_2), 27.8 (s, $C^{\alpha}H$), 31.6 (s, $C^{\beta}H_2$), 33.4 (s, Me, CMe_2), 45.1 (s, CH_2Ar), 51.2 (s, *C*Me_2), 60.9 (s, CH_2O), 120.6 (q, CF_3SO_3, $^{1}J_{CF}$ = 320.5 Hz), 125.4 (s, CH, C4), 127.2 (s, CH, C5), 128.1 (s, *m*-CH, Xy), 128.4 (s, *m*-CH, Xy), 129.4 (s, CH, C6), 130.4 (s, *p*-CH, Xy), 130.7 (s, *p*-CH, Xy), 132.4 (s, CH, C3), 134.4 (s, C2), 135.4 (s, *o*-C, Xy), 136 (s, *o*-C, Xy), 139.3 (br s, CN), 141.5 (s, C1), 144.3 (br s, CN), 176.4 (s, CO). The ^{13}C NMR resonances corresponding to *i*-C of both Xy groups are not observed.

Single Crystal X-ray Structure Determinations. Relevant crystallographic data and details of the refinements for the structures of compounds **2a**·$CHCl_3$, **2b-1**, **2d-3**·1/3CH_2Cl_2, **2e-4**·1/2$CHCl_3$, **3d**, **3g**, **6**, and **7e-HOTf** are given in Table 1 and 2. *Data Collection*. Crystals suitable for X-ray diffraction were mounted in inert oil on a glass fiber and transferred to a Bruker SMART diffractometer. Data were recorded at 100(2) K using graphite-monochromated Mo-Ka radiation (λ = 0.71073 Å) and ω-scan mode. Multi-scan absorption corrections were applied for all complexes. *Structure Solution and Refinements*. Crystal Structures were solved by the direct method and all non hydrogen atoms refined anisotropically on F^2 using the program SHELXL-97.[71] Hydrogen atoms were refined as follows: Compounds **2a**·$CHCl_3$, **2b-1**, **2d-3**·1/3CH_2Cl_2, **6** and **7e-HOTf**: NH or/and NH_2, free; methyl, rigid group; all others, riding. Complexes **2e-4**·1/2$CHCl_3$, **3d** and **3g**: NH_2, free with SADI; methyl, rigid group; all others, riding. Special features: Complex **2a**·$CHCl_3$: the chloroform is disordered over two positions with a ca. 69:31 occupancy distribution. **2e-**

4·1/2$CHCl_3$: the half molecule of chloroform is disordered over two positions with a ca. 50:50 occupancy distribution. **3d**: the CO_2Et group is disordered over two positions with a ca. 52:48 occupancy distribution.

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Supporting Information Available. Torsion angles of the eight-membered rings in compounds **2a**·$CHCl_3$, **2b-1**, **2d-3**·1/3CH_2Cl_2 and **2e-4**·1/2$CHCl_3$, selected ^1H and ^{13}C NMR data for the new compounds, details (including symmetry operators) of hydrogen bondings and listing of all refined and calculated atomic coordinates, anisotropic thermal parameters, bond lengths and angles and CIF files for compounds **2a**·$CHCl_3$, **2b-1**, **2d-3**·1/3CH_2Cl_2, **2e-4**·1/2$CHCl_3$, **3d**, **3g**, **6** and **7e-HOTf**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Table 1. Crystal Data and Structure Refinement Details for Complexes **2a**·$CHCl_3$, **2b-1**, **2d-3**·1/3CH_2Cl_2, and **2e-4**·1/2$CHCl_3$

	2a·$CHCl_3$	**2b-1**	**2d-3**·1/3CH_2Cl_2	**2e-4**·1/2$CHCl_3$
formula	$C_{18}H_{26}BrCl_3N_2OPd$	$C_{20}H_{27}ClN_2OPd$	$C_{19.33}H_{33.67}Cl_{1.67}N_2O_2Pd$	$C_{26.5}H_{33.5}Cl_{2.5}N_2Pd$
fw	579.07	453.29	491.63	575.08
temp (K)	100(2)	100(2)	100(2)	100(2)
cryst habit	colorless prism	yellow needle	yellow prism	yellow block
cryst size (mm)	0.38 x 0.07 x 0.06	0.21 x 0.09 x 0.06	0.31 x 0.19 x 0.07	0.35 x 0.29 x 0.17
cryst syst	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	13.7835(7)	8.2796(4)	11.1431(5)	8.9523(7)
b (Å)	7.7422(4)	17.1677(8)	18.3285(8)	11.2509(9)
c (Å)	22.1079(12)	27.9086(13)	18.4872(8)	13.0758(11)
α (deg)	90	90	60.820(2)	86.830(2)
β (deg)	02.136(2)	90.535(2)	88.523(2)	76.836(2)
γ (deg)	90	90	89.449(2)	86.417(2)
V (Å^3)	2306.5(2)	3966.8(3)	3295.5(3)	1278.76(18)
Z	4	8	6	2
ρ_{calcd} (Mg m^{-3})	1.668	1.518	1.486	1.494
μ(Mo, Kα) (mm^{-1})	2.894	1.080	1.063	1.004
F(000)	1152	1856	1524	590
θ range (deg)	1.60–28.23	1.88–28.29	1.83–28.19	1.82–28.60
no. rflns collected	25 736	45 462	38 363	15 848
no. indep rflns	5354	9177	14 783	6000
R_{int}	0.0302	0.0457	0.0247	0.0142
max, min transmsn	0.845, 0.636	0.938, 0.832	0.929, 0.647	0.848, 0.717
no. of restraints/params	77/274	2/475	18/754	7/304
goodness of fit on F^2	1.039	1.111	1.037	1.068
R1 ($I > 2\sigma(I)$)	0.0287	0.0381	0.0310	0.0299
wR2 (all rflns)	0.0746	0.0796	0.0790	0.0729
largest diff peak, hole (e Å^{-3})	0.765, –0.746	0.801, –0.632	0.895, –1.234	1.953, –0.944

Table 2. Crystal Data and Structure Refinement Details for Compounds **3d**, **3g**, **6** and **7e-HOTf**

	3d	**3g**	**6**	**7e-HOTf**
formula	$C_{30}H_{42}Cl_2N_2O_4Pd$	$C_{36}H_{42}Cl_2NPd$	$C_{28}H_{29}ClNPPd$	$C_{27}H_{33}F_3N_2O_3S$
fw	671.96	680.02	552.34	522.61
temp (K)	100(2)	100(2)	100(2)	100(2)
cryst habit	colorless needle	yellow prism	colorless block	colorless prism
cryst size (mm)	0.25 x 0.04 x 0.04	0.16 x 0.09 x 0.06	0.22 x 0.17 x 0.06	0.35 x 0.15 x 0.11
cryst syst	triclinic	triclinic	triclinic	triclinic
space group	$P\ \bar{1}$	$P\ \bar{1}$	$P\ \bar{1}$	$P\ \bar{1}$
a (Å)	5.9788(8)	6.0466(5)	9.9381(3)	9.6895(8)
b (Å)	9.4650(12)	10.1257(8)	11.6534(4)	10.3646(8)
c (Å)	14.2252(18)	13.9180(11)	12.6531(4)	13.2662(12)
α (deg)	80.693(2)	101.558(2)	98.737(2)	90.106(2)
β (deg)	89.281(2)	96.832(2)	108.481(2)	106.203(2)
γ (deg)	74.993(2)	104.834(2)	113.649(2)	103.980(2)
V (Å^3)	766.94(17)	793.89(11)	1205.64(7)	1238.05(18)
Z	1	1	2	2
ρ_{calcd} (Mg m^{-3})	1.455	1.422	1.521	1.402
μ(Mo, Kα) (mm^{-1})	0.816	0.780	0.963	0.186
F(000)	348	352	564	552
θ range (deg)	2.26–28.20	2.14–28.15	2.01–28.12	2.03–28.71
no. rflns collected	8928	9186	13 985	15 496
no. indep rflns	3448	3551	5394	5821
R_{int}	0.0409	0.0218	0.0168	0.0206
max, min transmsn	0.968, 0.822	0.955, 0.885	0.944, 0.816	0.980, 0.816
no. of restraints/params	1/188	1/197	25/299	0/337
goodness of fit on F^2	1.056	1.082	1.063	1.030
R1 ($I > 2\sigma(I)$)	0.0401	0.0271	0.0235	0.0394
wR2 (all rflns)	0.0850	0.0657	0.0573	0.1012
largest diff peak, hole (e Å^{-3})	0.676, –0.428	0.803, –0.241	0.423, –0.288	0.461, –0.376

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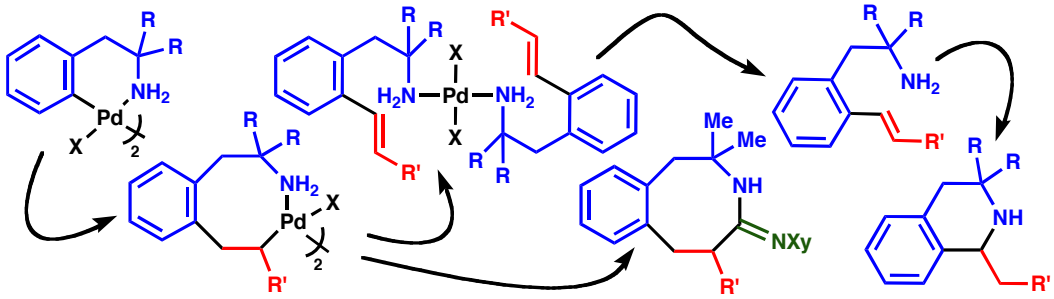

Ortho-palladated phenethylamine and phentermine react with olefins to give isolable and stable alkyl Pd(II) complexes containing β-hydrogens that can be used to prepare the corresponding ortho-vinylidated arylakylamines, tetrahydroisoquinolines or eigth-membered cyclic amidine derivatives