Palladium-Assisted Formation of Carbon−Carbon Bonds. Part 10.[1] Insertion Reactions of Isocyanides into the Pd−C Bond of Orthopalladated Primary Amines. Synthesis of 2-R-Aminoisoindolinium Salts (R = ^{t}Bu, 2,6-Xylyl)

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The palladated primary amines [Pd{$C_6H_3CH_2NH_2$-2-X-5}(μ-Br)]$_2$ [X = H (**1a**), OMe (**1b**), NO_2 (**1c**), F (**1d**)] react with isocyanides (Pd:RNC = 1:1) to give [Pd{$C_6H_3CH_2NH_2$-2-X-5}-Br(RNC)] [R = Xy = $C_6H_3Me_2$-2,6, X = H (**2a**), OMe (**2b**), NO_2 (**2c**), F (**2d**), R = ^{t}Bu, X = H (**3a**), OMe (**3b**), NO_2 (**3c**), F (**3d**)]. When XyNC reacts with **1a** (Pd:RNC = 1:2) or with **2a** (Pd:RNC = 1:1), the complex [Pd{(C=NXy)$C_6H_4CH_2NH_2$-2}(XyNC)Br] (**4a**) is obtained. The reactions of complexes **1** with isocyanides in the ratio Pd:RNC = 1:3 lead to Pd(I) complexes [$Pd_2Br_2L_4$] [L = XyNC (**5**); L = ^{t}Bu (**6**)]. On the basis of NMR data we propose the following reaction pathway for this reduction process: (1) formation of the corresponding monomer **2** or **3**, (2) insertion of one molecule of the isocyanide into the Pd−C bond of **2** or **3** to give [Pd{(C=NR)$C_6H_3CH_2NH_2$-2-X-5}(RNC)Br], (3) cleavage of the N−Pd bond and coordination of a new isocyanide molecule to give complexes [Pd{(C=NR)$C_6H_3CH_2NH_2$-2-X-5}$(RNC)_2$Br] [detected in solution for R = Xy, X = H (**7a**) and isolated as an acetylated derivative of this complex [Pd{(C=NXy)$C_6H_4CH_2NHC(O)Me$-2}$(XyNC)_2$Br] (**8a**)], and (4) decomposition of these complexes to give **5** or **6**. The organic product of these reactions was not identified. By refluxing mixtures of complexes **1** with RNC and TlOTf (Pd:RNC:TfO = 1:1:1) the corresponding isoindolinium triflates **9·OTf** [R = Xy, X = H (**9a·OTf**), OMe (**9b·OTf**), F (**9d·OTf**)] or **10·OTf** [R = ^{t}Bu, X = H (**10a·OTf**), OMe (**10b·OTf**), F (**10d·OTf**)] were isolated and characterized. A mechanism of formation of these isoindolinium triflates is proposed. When the reaction between **1a** and XyNC (Pd:RNC = 1:1) was carried out in refluxing toluene in the absence of TlOTf, or when **2a** was refluxed in toluene, an insertion of the isocyanide occurs in both cases to give [Pd{(C=NXy)$C_6H_4CH_2NH_2$-2}Br]$_2$ (**11**). If **1a** or **2a** is reacted with XyNC (Pd:RNC = 1:1.25 or 1:0.25, respectively), the complex [$PdBr_2${2-(XyNH)-isoindole}$_2$] (**12**) is formed. A proposal for the reaction pathway of this process is discussed. The crystal structures of **3d**, **9a·OTf**, and **12** have been determined.

Introduction

Insertion reactions of orthopalladated amines with unsaturated reagents such as alkenes[2−7] or alkynes[8−26] are well known. Since depalladation of the resulting complexes can afford interesting organic compounds,

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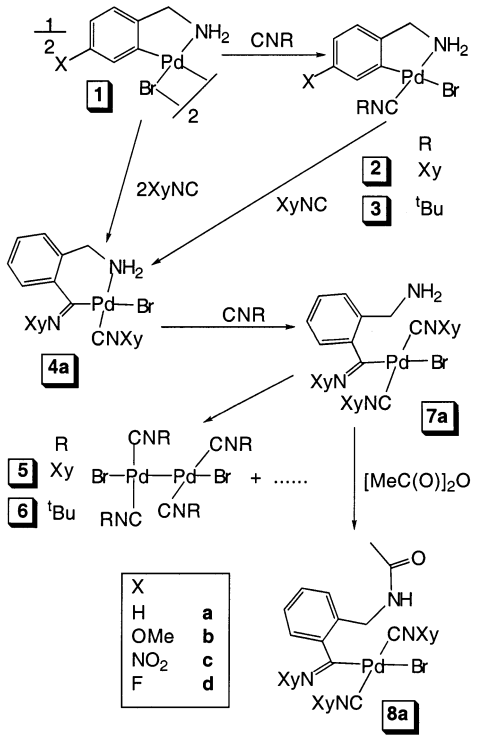
they have attracted great interest in organic synthesis.[2−15,27−39] Most of these insertion reactions involve cyclopalladated tertiary benzylamines, while only a few are devoted to primary amines,[23,24,27] because general syntheses of such cyclopalladated complexes have been only recently reported.[24,40−42] However, the number of studies on the reactivity of orthopalladated amines with isocyanides or carbon monoxide is very limited.[27,28,43−45] We have reported sequential insertion reactions of alkynes and CO or isocyanides into cyclopalladated secondary benzylamines,[25] whereas here we report the reactivity of cyclopalladated primary benzylamines toward isocyanides. A preliminary communication by Parkins et al. described the only previously reported reactions of a cyclopalladated primary amine with isocyanides.[27] In this paper, we study the reactions between various palladated primary amines and isocyanides at room temperature and in refluxing toluene under different molar ratios of complex to isocyanide.

Scheme 1



Some intermediates have been isolated, allowing the proposal of reasonable reaction pathways for these reactions that lead to the formation of 2-aminoisoindoles, isolated as their triflate salts or coordinated to palladium(II).

Results and Discussion

Room-Temperature Reactivity of Cyclopalladated Primary Benzylamines toward Isocyanides. By reacting at room temperature the dimeric complexes $[Pd\{C_6H_3CH_2NH_2\text{-}2\text{-}X\text{-}5\}(\mu\text{-}Br)]_2$ [X = H (**1a**), OMe (**1b**), NO_2 (**1c**), F (**1d**)] with isocyanides in the ratio Pd:RNC = 1:1, the halogen bridges are cleaved and the monomeric compounds $[Pd\{C_6H_3CH_2NH_2\text{-}2\text{-}X\text{-}5\}Br(RNC)]$ (**2**, **3**) [R = Xy = $C_6H_3Me_2$-2,6, X = H (**2a**), OMe (**2b**), NO_2 (**2c**), F (**2d**); R = ^{t}Bu, X = H (**3a**), OMe (**3b**), NO_2 (**3c**), F (**3d**)] are obtained (Scheme 1). The IR spectra of complexes **2** and **3** show the ν(C≡N) stretching frequencies [2180 and 2200 cm^{-1}, respectively] close to those of related complexes.[28,44,46] Furthermore we have determined the structure of **3d** by X-ray diffraction (see below).

By reacting **1a** or **2a** with XyNC (Pd:XyNC = 1:2 or 1:1, respectively) the complex resulting from monoinsertion of the isocyanide into the Pd−C bond $[Pd\{(C{=}NXy)C_6H_4CH_2NH_2\text{-}2\}(XyNC)Br]$ (**4a**) was isolated. The ^{1}H, ^{13}C NMR and IR data of **4a** agree with those found in similar insertion products.[44,47] Our proposal for its structure is based on the X-ray crystal structure of $[Pd\{C(=NR)(C_6H_4)(CH_2NMe_2)_2\}Br(RNC)]$ (R = ^{n}Bu).[44]

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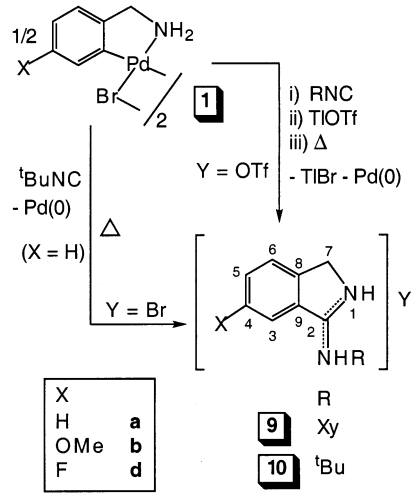
Complex **4a** reacts with 1 equiv of XyNC to give the dinuclear palladium(I) complex $[Pd_2Br_2(CNXy)_4]$ (**5**). Similar decomposition reactions occurred when compounds **1** were reacted at room temperature with a larger amount of the isocyanide (Pd:XyNC = 1:3), giving complexes $[Pd_2Br_2L_4]$ [L = XyNC (**5**), ^{t}BuNC (**6**)]. Complexes **5** and **6** were isolated from **1c** or **1a**, respectively, at room temperature. These reactions are similar to that of $[PdI(CH_2Ph)(^t BuNC)_2]$ with further ^{t}BuNC to give $[Pd_2I_2(^t BuNC)_4]$.[48] The IR and ^{1}H NMR data of compound **6** agree with those previously reported.[48] The characteristic spectroscopic data of **5**, which has been mentioned recently by Mingos,[49] are the signals at δ 2.53 ppm in the ^{1}H NMR spectrum and the intense band at 2156 cm^{-1} in the IR spectrum corresponding to ν(C≡N). We have also prepared **5** by reacting $[Pd(dba)_2]$ (dba = dibenzylidenacetone), XyNC, and *ortho*-bromobenzaldehyde (2:8:3 molar ratio) in refluxing toluene and determined its crystal structure.[50]

Mechanism of Formation of Palladium(I) Complexes $[Pd_2Br_2(CNR)_4]$. It is reasonable to assume that formation of **5** or **6** from **1** occurs via complex **2** or **3**, respectively, and $[Pd\{(C{=}NR)C_6H_3CH_2NH_2\text{-}2\text{-}X\text{-}5\}(RNC)Br]$ [R = Xy, X = H (**4a**), OMe, NO_2, F; R = ^{t}Bu, X = H, OMe, NO_2, F]. The formation of **5** by treatment of **4a** in dichloromethane with 1 equiv of XyNC for 12 h further supports the intermediacy of **4a** in the synthesis of **5** from **2a**. To find out more details about the mechanism of the formation of **5**, we monitored by ^{1}H NMR spectroscopy the reaction of **4a** with 1 equiv of XyNC in $CDCl_3$. After 10 min, **4a** had disappeared and two 2:1 singlets at 2.29 and 2.14 ppm corresponding to the Me groups of XyNC suggest the formation of a complex such as $[Pd\{(C{=}NXy)C_6H_4CH_2NH_2\text{-}2\}(XyNC)_2Br]$ (**7a**), resulting from cleavage of the N−Pd bond and coordination of a new isocyanide molecule. A triplet at 3.89 ppm and a broad signal at 3.70 ppm could be assigned to the CH_2 and NH_2 groups, respectively. A broad resonance at 2.38 ppm revealed the presence of **5**. After 20 min, the spectrum does not change significantly. Unfortunately, our attempts to isolate the proposed intermediate **7a** failed. Thus, if the solvent is removed from the reaction mixture after 10 min, the only isolated complex is **4a**, suggesting that it is in equilibrium with **7a** and that such equilibrium reverts to the left when trying to isolate **7a**. If the reaction time is 4 h, mixtures consisting of **4a** and **5** were obtained. However, we could isolate the acetylated derivative $[Pd\{C(=NXy)C_6H_4CH_2NHC(O)Me\text{-}2\}Br(XyNC)_2]$ (**8a**) by reacting a mixture of **4a** and XyNC with acetic anhydride. The instability of **8a** caused it to be contaminated with traces of **5**. This prevented correct elemental analyses and a ^{13}C NMR spectrum. However, the ^{1}H NMR resonances not due to the traces of **5** are in accordance with the structure proposed for **8a**. A different reaction pathway has been found in the reaction between $[PdCl(Me)(L_2)]$ (L_2 = 2,2′-bipyridine, 1,10-phenanthroline) and ^{t}BuNC or XyNC in acetonitrile. The insertion of the isocyanide into the Pd−Me bond occurs through a cationic intermediate that results after substitution of the chloro ligand by the isocyanide.[51]

Scheme 2



We have also studied by ^{1}H NMR spectroscopy the reaction of **2a** with 2 equiv of XyNC in $CDCl_3$. The ^{1}H NMR spectrum measured immediately after the mixture of reagents showed resonances due to **2a** and **7a**. After 10 min, complex **2a** had disappeared and signals appeared corresponding to **7a** and **5**. Two new resonances at 2.26 and 4.80 ppm and that corresponding to **5** grew with time, while the intensity of the signals corresponding to **7a** decreased. After 2.5 days, the signals corresponding to **7a** had disappeared, while those corresponding to **5** and those at 2.26 and 4.80 ppm remained. These two resonances could be due to Me and CH_2 protons of some 2-aminoisoindolinium salt or 2-aminoisoindoline or some related derivative.

Reactions of Complexes 1 toward Isocyanides in Refluxing Toluene in the Ratio Pd:RNC = 1:1. Synthesis of Isoindolinium Salts. A preliminary communication by Parkins et al. in 1984 described the reactions of $[Pd\{C_6H_4CH_2NH_2\text{-}2\}(RNC)I]$ and RNC (R = ^{t}Bu, Ph) (1:1 molar ratio) in refluxing toluene. The corresponding isoindolinium iodides and their free bases were characterized by IR and NMR spectroscopies.[27] The present availability of cyclopalladated primary amines prompted us to extend this work, starting from our bromo complexes **1a**−**d**. Thus, by refluxing a toluene solution of **1a** with ^{t}BuNC (Pd:^{t}BuNC = 1:1), an intractable mixture of 2-aminoisoindolinium bromide **10a·Br** (characterized by comparing its ^{1}H NMR spectrum with that of **10a·OTf**; see below and Scheme 2) and colloidal Pd(0) was obtained. Under the same thermal conditions, complex **1a** reacts differently with XyNC (Pd:XyNC = 1:1) to give the dimer $[Pd\{(C{=}NXy)C_6H_4CH_2NH_2\text{-}2\}Br]_2$ (**11**) (Scheme 3). By refluxing a toluene suspension of **2a** complex **11** was also obtained. Similar insertion reactions have been observed on heating other (isocyanide)(aryl)palladium complexes.[28,52] Due to the insolubility of **11** in common organic solvents, no NMR data are available. However, the structure proposed for **11** is based on its reaction with XyNC to give **4a** and on those determined by X-ray crystallography of related complexes.[52−55]

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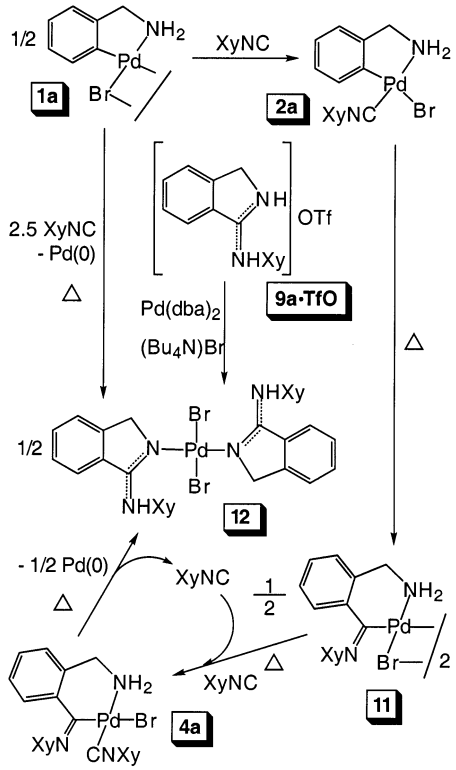
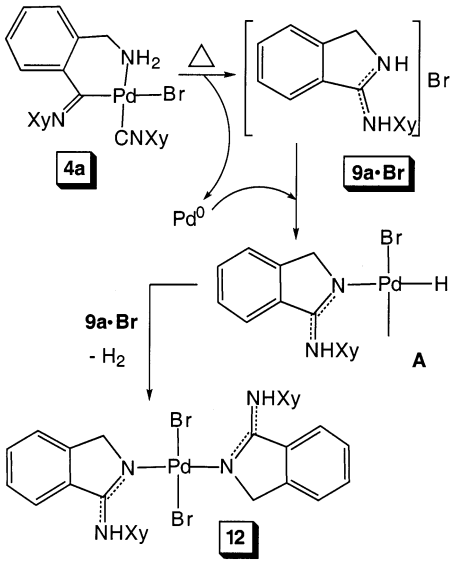
Scheme 3



We were successful in isolating the triflate salts **9a·OTf** (OTf = O_3SCF_3) and **10a·OTf**, as well as the substituted derivatives **9b·OTf**, **9d·OTf**, **10b·OTf**, and **10d·OTf**, by refluxing in toluene for 1 h mixtures containing the corresponding complex **1**, RNC, and TlOTf (Pd:RNC:TfO = 1:1:1) (Scheme 2). To remove the colloidal Pd(0) formed, it was surprisingly helpful to reflux the reaction mixture with NaBr for one more hour. The organic compounds **9** and **10** were fully characterized and, additionally, the X-ray crystal structure of **9a·OTf** was determined (see below). All reactions starting from **1c** gave complex mixtures.

Mechanism of Formation of 2-Aminoisoindolinium Salts 9 and 10. In agreement with the above results, it is reasonable to assume that complexes **1** react with isocyanides in refluxing toluene to give the adducts **2** or **3**. Under these conditions the coordinated isocyanide would insert into the C−Pd bond to give inserted species such as **11**. In the case of the reaction of **1a** with ^{t}BuNC the inserted complex [Pd{(C=N^{t}Bu)-$C_6H_4CH_2NH_2$-2}Br]$_2$ would be unstable, decomposing to give **10a·Br** and palladium metal. Contrarily, the reaction of **1a** with XyNC would give the stable complex **11**. The iodo complex used by Parkins would give less stable inserted complexes than our bromo complexes and would give directly 2-aminoisoindolinium salts and palladium metal.[27] Similarly, the instability of the triflato derivatives of the inserted complexes obtained when complexes **1** were reacted with isocyanides in the presence of thallium triflate would explain the formation of salts **9** and **10**.

Scheme 4



Reaction of Complex 1a with XyNC in Refluxing Toluene in the Ratio Pd:RNC = 1:1.25. Synthesis and Mechanism of Formation of [PdBr$_2${2-(XyNH)-isoindole}$_2$] (12). If reaction of **1a** with XyNC in refluxing toluene is carried out in the ratio Pd:RNC = 1:1.25, a completely different result is obtained; palladium metal and complex [PdBr$_2${2-(XyNH)-isoindole}$_2$] (**12**) were formed (Scheme 3). The same result is obtained if **2a** is refluxed in toluene with XyNC in the ratio Pd:RNC = 1:0.25.

As **12** is also formed when **11** is refluxed in toluene with XyNC (1:0.2 molar ratio), it is reasonable to conclude (i) that **11** is an intermediate in the synthesis of **12** from **1a** (or **2a**) and XyNC and (ii) that XyNC is required to decompose **11** into palladium metal and **12**, despite not being stoichiometrically necessary. The following experiment could explain this requirement. The room-temperature reaction between **11** and XyNC in an 1:2 molar ratio affords **4a**, previously prepared by reacting **1a** or **2a** with XyNC at room temperature (see above). Complex **4a** decomposes in refluxing toluene, giving palladium metal and **12**. Therefore, it is reasonable to assume that formation of **12** requires the generation and decomposition in refluxing toluene of **4a**. Because such decomposition releases the isocyanide required to transform **11** into **12**, the complex **4a** and the excess of isocyanide play the role of a catalyst in the synthesis of **12** from **1a**, **2a**, or **11**.

The isoindole ligand in **12** is the result of a C−N coupling process that requires a reduction of the metal center. In fact, we observed the formation of Pd metal in the thermal decomposition of **4a** to give **12**. Therefore, we describe here a rare example of a reaction in which the organic compound resulting from a reductive elimination appears in the final product coordinated to Pd(II). It is reasonable to assume that the required oxidation of Pd(0) to Pd(II) to give **12** occurred through an oxidative addition reaction of the isoindolinium salt **9a·Br** to Pd(0) (Scheme 4), both formed in the decomposition of **4a**, to give **A**, a hydrido(isoindole)palladium(II) complex. One iminium salt has been found to react

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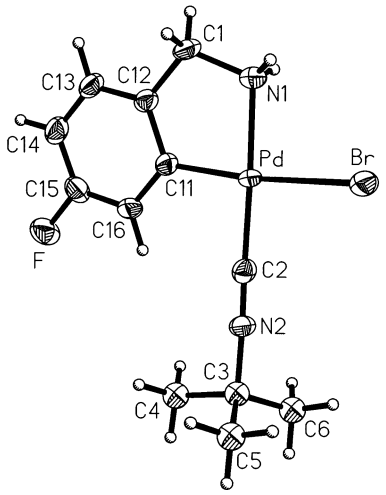

Figure 1. Thermal ellipsoid plot (50% probability level) of **3d**. Selected bond lengths (Å) and angles (deg): Pd−C(2) 1.927(3); Pd−C(11) 1.990(3); Pd−N(1) 2.053(3); Pd−Br 2.5127(4); N(1)−C(1) 1.482(4); N(2)−C(2) 1.153(4); N(2)−C(3) 1.460(3); C(2)−Pd−C(11) 94.24(12); C(11)−Pd−N(1) 82.02(11); C(2)−Pd−Br 91.88(8); N(1)−Pd−Br 91.93-(8); C(1)−N(1)−Pd 112.26(19); N(1)−C(1)−C(12) 108.0(2); C(2)−N(2)−C(3) 175.3(3); N(2)−C(2)−Pd 178.4(3).

with a Ni(0) complex to give a hydrido(imino)nickel(II) complex.[56] In addition, the isolation of hydrido complexes $[PdCl(H)L_2]$ (L = PPh_3, PCy_3) by reacting PdL_n with HCl at low temperature has been reported.[57,58] The reaction of the hydrido complex **A** with **9a·Br** could lead to **12** and H_2 (Scheme 4). The reactions of $[M(PPh_3)_4]$ (M = Ni, Pd) with HX acids have been reported to give $[PdCl_2(PPh_3)_2]$ and H_2 through the same hydrido complexes isolated at low temperature.[59] The stoichiometry of this reaction requires, as observed, half the Pd(0) to remain unreacted. To support our proposal of a mechanism for the synthesis of **12**, we reacted **9a·OTf** with the Pd(0) complex $[Pd(dba)_2]$ and an excess of Bu_4NBr in refluxing toluene and isolated complex **12**.

We have unsuccessfully attempted to prepare **9a·OTf** by reacting ($IC_6H_4CH_2NH_3$-2)OTf with XyNC and Et_3N (1:1:1 molar ratio) in refluxing toluene using as catalyst the product of the reaction of **2a** with TlOTf in acetone (molar ratio of reagents to catalyst = 10:1). The salt ($IC_6H_4CH_2NH_3$-2)OTf was used instead of $IC_6H_4CH_2$-NH_2-2 because this product is of low stability. We report the details of the synthesis of both iodo derivatives starting from commercial $IC_6H_4CH_2CO_2H$-2 (see Supporting Information).

Crystal Structures. The crystal structures of **3d** (Figure 1), **9a·OTf** (Figure 2), and **12** (Figure 3) have been determined. Complex **3d** shows a distorted square-planar coordination around the palladium atom. The mean deviation from the plane Pd, N(1), C(11), C(2), and Br is 0.034 Å. The isocyanide is in *cis* position with respect to the aryl ligand. This geometry is in agreement with the greater *transphobia* between two carbon donor ligands than between a C and an N donor ligand.[60] In the asymmetric unit, molecules of **3d** associate through intermolecular N−H···Br hydrogen bonds (see Table 1), forming ribbons parallel to the *x* axis (Figure 4). In the salt **9a·OTf** the interplanar angle between the two ring systems is 68°. The classical H bonds NH···O connect the ions in spiral chains parallel to the *y* axis. The three nonclassical CH···O bonds link these chains to form a three-dimensional network (Table 1). Figure 5 shows all the H bonds formed by one cation. In complex **12** the ligands are in a square-planar coordination around

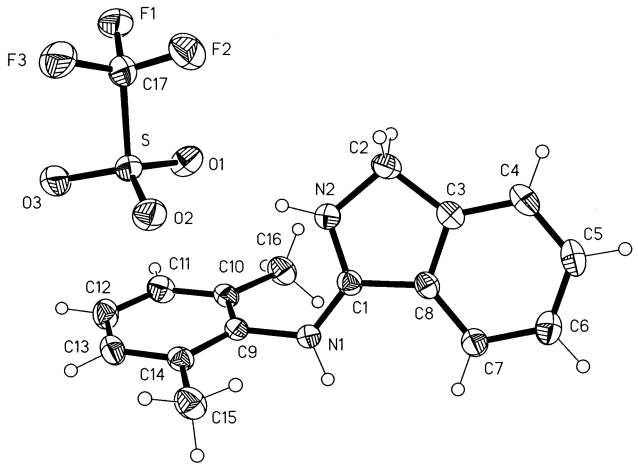

Figure 2. Thermal ellipsoid plot (50% probability level) of **9a·OTf**. Selected bond lengths (Å) and angles (deg): N(1)−C(1) 1.3237(18); N(1)−C(9) 1.4494(17); N(2)−C(1) 1.3226(18); N(2)−C(2) 1.4646(19); C(1)−C(8) 1.4602(19); C(2)−C(3) 1.503(2); C(3)−C(8) 1.3955(19); C(1)−N(1)−C(9) 123.64(12); C(1)−N(2)−C(2) 112.64(12); N(2)−C(1)−N(1) 124.90(13); N(2)−C(1)−C(8) 109.02(12); N(1)−C(1)−C(8) 126.06(13); N(2)−C(2)−C(3) 101.98(11).

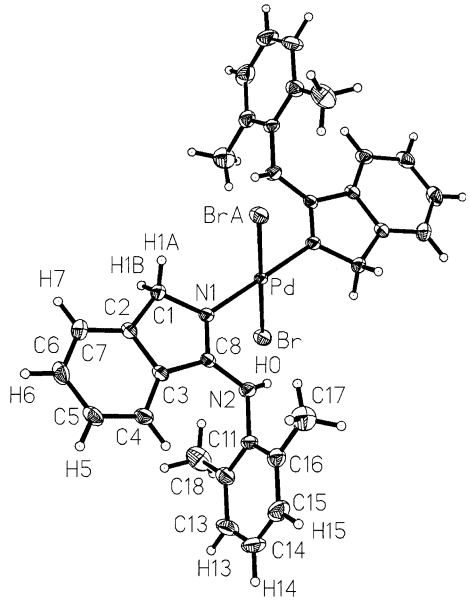

Figure 3. Thermal ellipsoid plot (50% probability level) of **12**. Selected bond lengths (Å) and angles (deg): Pd−N(1) 2.011(2); Pd−Br 2.4226(3); N(1)−C(8) 1.306(3); N(1)−C(1) 1.466(3); N(2)−C(8) 1.339(3); N(2)−C(11) 1.435(3); C(1)−C(2) 1.498(3); C(2)−C(3) 1.395(4); C(3)−C(8) 1.478(3); N(1)−Pd−Br 90.75(6); N(1)−Pd−Br#1 89.24(6); C(8)−N(1)−C(1) 110.1(2); C(8)−N(1)−Pd 127.5(2); C(1)−N(1)−Pd 122.1-(2); C(8)−N(2)−C(11) 124.9(2); N(1)−C(8)−N(2) 122.8(2); N(1)−C(8)−C(3) 111.4(2); N(2)−C(8)−C(3) 125.8(2).

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Table 1. Hydrogen Bonds [Å and deg] for 3d[a] and 9a·OTf[b]

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	∠(DHA)
3d				
N(1)−H(1)···Br#1	0.83(3)	2.65(3)	3.433(3)	158(4)
N(1)−H(2)···Br#2	0.82(2)	2.77(3)	3.458(3)	144(3)
9a·OTf				
N(2)−H(02)···O(1)	0.877(19)	1.95(2)	2.8115(17)	166.1(17)
N(1)−H(01)···O(2)#1	0.895(17)	1.976(17)	2.8561(16)	167.3(15)
C(2)−H(2B)···O(1)#2	0.99	2.47	3.3578(19)	149.1
C(7)−H(7)···O(3)#1	0.95	2.59	3.4288(19)	146.7
C(11)−H(11)···O(3)#3	0.95	2.51	3.4442(18)	169.5

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+1, -z+2$; #2 $-x+2, -y+1, -z+2$. [b] Symmetry transformations used to generate equivalent atoms: #1 $-x+1/2, y+1/2, -z+1/2$; #2 $-x+1, -y+1, -z$; #3 $-x+3/2, y+1/2, -z+1/2$.

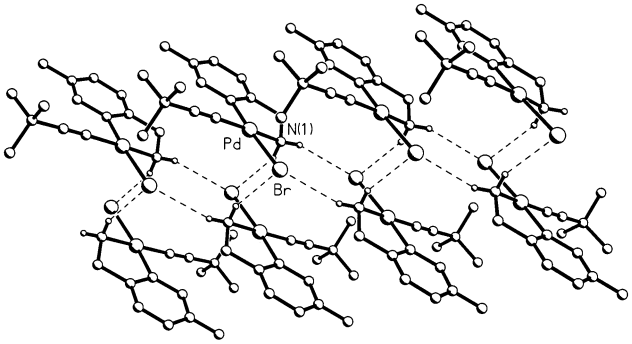

Figure 4. View of the hydrogen bond interactions in **3d**.

the palladium atom (Figure 3). The Pd−Br bond length [2.4226(3) Å] is normal [mean value of 59 *trans*-dibromopalladium complexes from CCDC: 2.430(3) Å]. The lower *trans* influence of a bromo than an aryl group explains the shorter Pd−Br bond length in **12** than in **3d** [2.5128(4) Å]. The Pd−N [2.011(2) Å] is also normal [mean value of 57 compounds containing the group Pd−N(C)=C−N from CCDC, 2.035(6) Å]. The similar N−C bond distances in the group N(1)−C(8)−N(2) [N(1)−C(8) 1.306(3), C(8)−N(2) 1.339(3) Å] and the significantly longer distances of N(1) and N(2) with their other neighbors [N(1)−C(1) 1.466(3), N(2)−C(11), 1.435(3) Å]

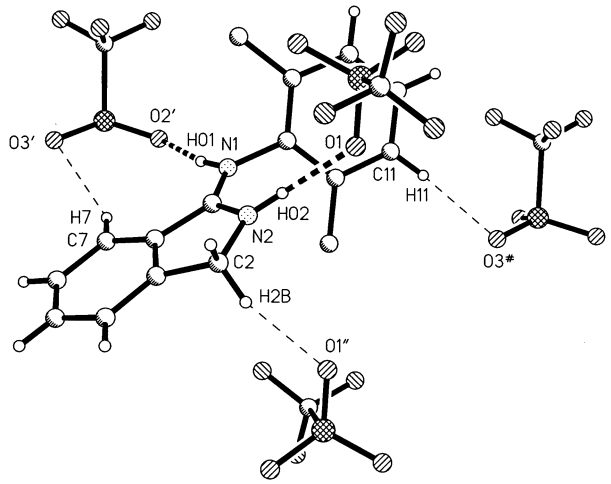

Figure 5. View of the hydrogen bond environment of the cation in **9a·OTf**.

suggest that a delocalization of electron density occurs between the atoms N(1), C(8), and N(2). The same occurs in the group N(1)−C(1)−N(2) of the salt **9a·OTf**. Additionally, the angles C(8)−N(2)−C(11) [124.9(2)°] in **12** and C(9)−N(1)−C(1) [123.64(12)°] in **9a·OTf** are far away from the expected sp^3 hybridization for N(2) and N(1), respectively, if a lone pair were assumed on these atoms. The N(1) in **12** is only slightly out of the plane Pd−C(1)−C(8) [the C(1)−N(1)−C(8) plane forms angles of 5.8° and 5.4° with Pd−N(1)−C(8) and Pd−N(1)−C(1) planes, respectively], indicating that the lone pair is marginally located on N(1). Probably, the two pairs of electrons (the lone and the π pairs) are delocalized over Pd−N(1)−C(8)−N(2) bonds. The atoms C(1), N(1), C(8), N(2), and C(3) are coplanar (mean deviation from the plane 0.01 Å).

Conclusions

The room-temperature reactions of cyclopalladated primary amines **1** with excess of isocyanides proceed through the following steps: (1) coordination of the isocyanide after bridge-splitting of the dimer, (2) insertion of a molecule of the isocyanide into the Pd−C bond of the resulting monomer, (3) coordination of a third isocyanide by cleavage of the Pd−NH_2 bond, and (4) a decomposition process that gives the Pd(I) complex [$Pd_2Br_2(RNC)_4$] and some 2-aminoisoindole derivative that could not be isolated.

The reactions in refluxing toluene of **1** with RNC and TlOTf (Pd:RNC:TfO = 1:1:1) lead to the corresponding 2-R-aminoisoindolinium triflates **9** and **10**. Similarly, **1a** reacts with ^{t}BuNC (Pd:^{t}BuNC = 1:1) in refluxing toluene to give 2-^{t}Bu-aminoisoindolinium bromide, **10a·Br**, which could not be fully separated from palladium(0). However, the reaction of **1a** with XyNC (1:2 molar ratio) in refluxing toluene gives the monoinserted complex **11**. The C−N coupling leading to isoindoles requires the use of an excess of XyNC, and the product finally obtained is complex **12**, in which two molecules of 2-aminoisoindole are coordinated to $PdBr_2$. We give experimental data that strongly suggest that the formation of this complex requires (1) coordination of a second molecule of isocyanide per palladium through a bridge-splitting process from complex **11**, (2) decomposition of

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the resulting complex **4a** to give 2-Xy-aminoisoindolinium bromide (**9a·Br**) and Pd(0), (3) an oxidative addition reaction between these two products to give a hydrido(bromo)(isoindole)palladium(II) complex, and (4) the reaction of this hydrido complex with **9a·Br** to give complex **12**.

Experimental Section

General Procedures. Infrared spectra were recorded on Perkin-Elmer 1430 and 16F-PC-FT spectrometers. NMR spectra were carried out with a Varian Unity 300 or a Bruker 200. Chemical shifts are referenced to TMS [^{1}H and ^{13}C{1H}]. The starting materials [Pd{$C_6H_3CH_2NH_2$-2-X-5}(μ-Br)]$_2$ (X = F, NO_2, OMe) were prepared as reported.[40] The preparation of $IC_6H_4CH_2NH_2$-2 and ($IC_6H_4CH_2NH_3$-2)OTf is reported in the Supporting Information.

Synthesis of [Pd{$C_6H_4CH_2NH_2$-2}(μ-Br)]$_2$ (1a). Benzylamine (488 μL, 4.46 mmol) was added to a suspension of [Pd(OAc)$_2$]$_3$ (1.00 g, 1.49 mmol) in 50 mL of acetone. The resulting solution was refluxed for 8 h. The reaction mixture was filtered, and NaBr (1.00 g) was added to the orange filtrate. The resulting suspension was stirred at room temperature overnight and evaporated to dryness. The residue was stirred with CH_2Cl_2 (30 mL) and filtered and the solid washed with water until the filtrates were colorless. After washing with Et_2O, the solid was dried in vacuo to give **1a** as a yellow solid. Yield: 558 mg, 43%. Dec pt: 187 °C. ^{1}H NMR [300 MHz, $(CD_3)_2SO$]: δ 3.94 (t, 4 H, CH_2, ^3J(H,H) = 5.3 Hz), 5.51 (br s, 4 H, NH_2), 6.66−7.70 (m, 8 H, C_6H_4). Anal. Calcd for $C_{14}H_{16}Br_2N_2Pd_2$: C, 28.75; H, 2.76; N, 4,79. Found: C, 29.11; H, 2.55; N, 4.55.

Synthesis of Complexes 2 and 3. RNC (R = Xy, ^{t}Bu) was added to a suspension of **1** in CH_2Cl_2. Within a few minutes a slightly yellow solution resulted, which was stirred at room temperature for 15 min. Concentrating the solution to a volume of ca. 2 mL and subsequent addition of diethyl ether afforded complexes **2** or **3** as colorless solids.

Synthesis of [Pd{$C_6H_4CH_2NH_2$-2}Br{XyNC}] (2a). 2a was obtained starting from **1a** (407 mg, 0.696 mmol) and XyNC (183 mg, 1.395 mmol) in CH_2Cl_2 (50 mL). Yield: 530 mg, 90%. Dec pt: 211 °C. IR (Nujol, cm^{-1}): ν 2178 (C≡N). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.50 (s, 6 H, Me), 3.99 (br s, 2 H, NH_2), 4.33 (t, 2 H, CH_2, ^3J(H,H) = 6.0 Hz), 6.88−7.40 (m, 7 H, C_6H_4 and C_6H_3). Anal. Calcd for $C_{16}H_{17}BrN_2Pd$: C, 45.26; H, 4.04; N, 6.60. Found: C, 45.22; H, 4.05; N, 6.80.

Synthesis of [Pd{$C_6H_3CH_2NH_2$-2-OMe-5}Br(XyNC)] (2b). 2b was obtained starting from **1b** (91 mg, 0.141 mmol) and XyNC (37 mg, 0.282 mmol) in CH_2Cl_2 (20 mL). Yield: 99 mg, 77%. Dec pt: 201 °C. IR (Nujol, cm^{-1}): ν 2184 (C≡N). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.53 (s, 6 H, Me), 3.71 (s, 3 H, OMe), 3.82 (br s, 2 H, NH_2), 4.29 (t, 2 H, CH_2, ^3J(H,H) = 6.0 Hz), 6.58 (dd, 1 H, H4, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 2.5 Hz), 6.95 (d, 1 H, H6, ^4J(H,H) = 2.5 Hz), 7.00 (d, 1 H, H3, ^3J(H,H) = 8.3 Hz), 7.11−7.23 (m, 3 H, C_6H_3). Anal. Calcd for $C_{17}H_{19}BrN_2OPd$: C, 45.01; H, 4.22; N, 6.17. Found: C, 45.09; H, 3.95; N, 6.13.

Synthesis of [Pd{$C_6H_3CH_2NH_2$-2-NO_2-5}Br(XyNC)] (2c). 2c was obtained starting from **1c** (116 mg, 0.171 mmol) and XyNC (45 mg, 0.343 mmol) in CH_2Cl_2 (20 mL). Yield: 120 mg, 74%. Dec pt: 209 °C. IR (Nujol, cm^{-1}): ν 2188 cm^{-1} (C≡N). NMR: the insolubility of **2c** in any common organic solvent prevented us from measuring its NMR spectra. Anal. Calcd for $C_{16}H_{16}BrN_3O_2Pd$: C, 41.01; H, 3.44; N, 8.97. Found: C, 40.86; H, 3.18; N, 8.97.

Synthesis of [Pd{$C_6H_3CH_2NH_2$-2-F-5}Br{XyNC}] (2d). 2d was obtained starting from **1d** (100 mg, 0.161 mmol) and XyNC (43 mg, 0.328 mmol) in CH_2Cl_2 (20 mL). Yield: 100 mg, 91%. Dec pt: 168 °C. IR (Nujol, cm^{-1}): ν 2180 (C≡N). ^{1}H NMR [200 MHz, $(CD_3)_2SO$]: δ 2.49 (s, 6 H, Me), 4.01 (br s, 2 H, CH_2), 5.44 (br s, 2 H, NH_2), 6.83−7.37 (m, 6 H, C_6H_3). Anal. Calcd for $C_{16}H_{16}BrFN_2Pd$: C, 43.52; H, 3.65; N, 6.34. Found: C, 43.67; H, 3.53; N, 6.19.

Synthesis of [Pd{$C_6H_4CH_2NH_2$-2}Br(^{t}BuNC)] (3a). 3a was obtained starting from **1a** (192 mg, 0.328 mmol) and ^{t}BuNC (74 μL, 0.655 mmol) in CH_2Cl_2 (20 mL). Yield: 205 mg, 83%. Dec pt: 130 °C. IR (Nujol, cm^{-1}): ν 2202 (C≡N). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.54 (s, 9 H, Me), 3.92 (br s, 2 H, NH_2), 4.20 (t, 2 H, CH_2, ^3J(H,H) = 5.6 Hz), 6.91−7.16 (m, 4 H, C_6H_4). Anal. Calcd for $C_{12}H_{17}BrN_2Pd$: C, 38.38; H, 4.56; N, 7.46. Found: C, 38.18; H, 4.47; N, 7.25.

Synthesis of [Pd{$C_6H_3CH_2NH_2$-2-OMe-5}Br{^{t}BuNC)] (3b). 3b was obtained starting from **1b** (74 mg, 0.115 mmol) and ^{t}BuNC (30 μL, 0.266 mmol) in CH_2Cl_2 (20 mL). Yield: 80 mg, 86%. Dec pt: 147 °C. IR (Nujol, cm^{-1}): ν 2200 (C≡N). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.58 (s, 9 H, Me), 3.76 (s, 3 H, OMe), 4.18 (t, 2 H, CH_2, ^3J(H,H) = 5.9 Hz), 6.61 (dd, 1 H, H4, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 2.4 Hz), 6.73 (d, 1 H, H6, ^4J(H,H) = 2.4 Hz), 6.97 (d, 1 H, H3, ^3J(H,H) = 8.4 Hz). The signal for NH_2 was overlapped by that of OMe. Anal. Calcd for $C_{13}H_{19}BrN_2OPd$: C, 38.49; H, 4.72; N, 6.91. Found: C, 38.17; H, 4.84; N, 6.96.

Synthesis of [Pd{$C_6H_3CH_2NH_2$-2-NO_2-5}Br(^{t}BuNC)] (3c). 3c was obtained starting from **1c** (79 mg, 0.116 mmol) and ^{t}BuNC (30 μL, 0.266 mmol) in CH_2Cl_2 (20 mL). Yield: 55 mg, 56%. Dec pt: 201 °C. IR (Nujol, cm^{-1}): ν 2210 (C≡N). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.60 (s, 9 H, Me), 4.19 (br s, 2 H, NH_2), 4.36 (t, 2 H, CH_2, ^3J(H,H) = 5.8 Hz), 7.18 (d, 1 H, H3, ^3J(H,H) = 8.3 Hz), 7.92 (dd, 1 H, H4, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 2.3 Hz), 7.99 (d, 1 H, H6, ^4J(H,H) = 2.3 Hz). Anal. Calcd for $C_{12}H_{16}BrN_3O_2Pd$: C, 34.27; H, 3.83; N, 9.99. Found: C, 34.52; H, 3.78; N, 9.66.

Synthesis of [Pd{$C_6H_3CH_2NH_2$-2-F-5}Br(^{t}BuNC)] (3d). 3d was obtained starting from **1d** (100 mg, 0.161 mmol) and ^{t}BuNC (37 μL, 0.328 mmol) in CH_2Cl_2 (20 mL). Yield: 112 mg, 89%. Dec pt: 137 °C. IR (Nujol, cm^{-1}): ν 2018 (C≡N). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.56 (s, 9 H, Me), 3.91 (br s, 2 H, NH_2), 4.23 (t, 2 H, CH_2, ^3J(H,H) = 5.8 Hz), 6.75 (dt, 1 H, H4, ^3J(F,H) = ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.5 Hz), 6.82 (dd, 1 H, H6, ^3J(F,H) = 9.2 Hz, ^4J(H,H) = 2.5 Hz), 7.01 (dd, 1 H, H3, ^3J(H,H) = 8.2 Hz, ^4J(F,H) = 5.6 Hz). Anal. Calcd for $C_{12}H_{16}BrFN_2Pd$: C, 36.62; H, 4.10; N, 7.12. Found: C, 36.62; H, 3.95; N, 6.85.

Synthesis of [Pd{C(=NXy)$C_6H_4CH_2NH_2$-2}Br(XyNC)]·1/2CH_2Cl_2 (4a). To a suspension of **2a** (233 mg, 0.550 mmol) in CH_2Cl_2 (50 mL) was added XyNC (80 mg, 0.610 mmol). The resulting solution was stirred at room temperature during 1.5 h and then was concentrated (ca. 1 mL). Upon addition of Et_2O, a solid crystallized, which is filtrated, washed with ether, and dried in vacuo to give pale yellow **4a**. Yield: 254 mg, 83%. Dec pt: 175 °C. IR (Nujol, cm^{-1}): ν 1634 (C=N), 2184 (C≡N). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.13, 2.29 (s, 12 H, Me), 3.49 (br s, 2 H, NH_2), 3.90 (t, 2 H, CH_2, ^3J(H,H) = 5.9 Hz), 6.77−7.57 (m, 10 H, C_6H_4, C_6H_3). ^{13}C NMR: (50 MHz, $CDCl_3$): δ 18.6, 19.1 (Me), 44.3 (CH_2), 123.4, 125.7 (CH), 126.8 (aromatic C), 127.7, 127.9, 128.5, 128.6, 129.4 (CH), 135.1, 135.4 (aromatic C), 150.8 (CN), 180.8 (C=N). Anal. Calcd for $C_{25.5}H_{27}BrClN_3Pd$: C, 51.28; H, 4.56; N, 7.04. Found: C, 51.27; H, 4.48; N, 7.11.

Synthesis of [Pd_2Br_2(XyNC)$_4$] (5). To a suspension of **1c** (123 mg, 0.199 mmol) in CH_2Cl_2 (30 mL) was added XyNC (156 mg, 1.19 mmol). The resulting mixture was stirred at room temperature overnight. The solvent was removed in vacuo, the solid was washed with Et_2O, and the resulting suspension was filtered. The yellow solid was dried in vacuo to give **5**. Yield: 93 mg, 52%. Dec pt: 228 °C. IR (Nujol, cm^{-1}): ν 2156 (C≡N). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.53 (s, 24 H, Me), 7.08−7.27 (m, 12 H, C_6H_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 19.2 (Me), 128.1 (*m*-C's of C_6H_3), 130.6 (*p*-C of C_6H_3) 135.7 (*o*-C's of C_6H_3), 143.0 (br, *i*-C of C_6H_3), the signal for XyN*C* was not observed. Anal. Calcd for $C_{36}H_{36}Br_2N_4Pd_2$: C, 48.19; H, 4.04; N, 6.24. Found: C, 48.24; H, 4.07; N, 6.34.

Synthesis of [$Pd_2Br_2(^tBuNC)_4$] (6). This yellow complex was obtained as **5** from **1a** (107 mg, 0.183 mmol) in CH_2Cl_2 (30 mL) and ^{t}BuNC (125 μL, 1.107 mmol). Yield: 98 mg, 76%. IR (Nujol, cm^{-1}): ν 2166 (C≡N). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.54 (s, 36 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 30.3 (Me), 58.2 (*C*Me_3), the signal for ^{t}Bu*N*C was not observed.

Synthesis of [Pd{C(=NXy)$C_6H_4CH_2$NHC(O)Me-2}Br-(XyNC)$_2$] (8a). To a solution of **4a** (52 mg, 0.094 mmol) in CH_2Cl_2 (40 mL) were added XyNC (20 mg, 0.152 mmol) and acetic anhydride (30 mL, 0.318 mmol), and the mixture was stirred at room temperature for 10 min. The solution was brought to dryness in vacuo, and the remaining oily residue was dissolved in CH_2Cl_2 (2 mL). After addition of *n*-hexane and filtration, complex **8a** was obtained as a pale yellow solid. Yield: 43 mg, 63%. IR (Nujol, cm^{-1}): ν 1614, 1634 (C=O, C=N), 2182 (C≡N), 3276 (NH). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.83 [s, 3 H, C(O)Me], 2.19 [s, 12 H, $C_6H_3(Me)_2$], 2.22 [s, 6 H, $C_6H_3(Me)_2$], 4.60 [d, ^3J(H,H) = 6.3 Hz, 2 H, CH_2], 6.98−7.53 (m, H, C_6H_4 + C_6H_3), 8.44 [d, br, 1 H, NHC(O)Me]. The instability of **8a** prevented us from recording its ^{13}C NMR spectrum and obtaining correct elemental analyses (see Discussion).

Synthesis of 9·OTf and 10·OTf. A stoichiometric amount of RNC (R = Xy, ^{t}Bu) was added to a suspension of **1** in acetone. Upon addition of TlOTf, immediate precipitation of TlBr occurred. The solvent was removed in vacuo, and the remaining residue was suspended in toluene and refluxed for 1 h, upon which Pd(0) precipitated. To the black reaction mixture was added NaBr (1.00 g) (see Discussion), and the mixture was refluxed for one more hour. After cooling to room temperature in the case of ^{t}BuNC, the toluene was removed in vacuo and the remaining black residue was suspended in CH_2Cl_2 and filtered through Celite. In the case of XyNC the toluene mixture was directly filtered through Celite. The filtrate was brought to dryness, the oily residue was dissolved in about 1 mL of CH_2Cl_2, and addition of Et_2O afforded compounds **10·OTf** and **9·OTf** as colorless solids.

Synthesis of [2-(XyNH)-isoindolinium]OTf (9a·OTf). 9a·OTf was obtained starting from **1a** (102 mg, 0.175 mmol), XyNC (46 mg, 0.351 mmol), and TlOTf (124 mg, 0.351 mmol). Yield: 55 mg, 41%. Mp: 170 °C. IR (Nujol, cm^{-1}): ν 1660 (C=N). ^{1}H NMR [300 MHz, $(CD_3)_2SO$]: δ 2.24 (s, 6 H, Me), 4.84 (s, 2 H, CH_2), 6.47−6.55 (m, 3 H, C_6H_3), 6.99−7.06 (m, 3 H, C_6H_4), 7.53−7.55 (m, 1 H, C_6H_4), 9.58 (s, 1 H, NH), 10.72 (s, 1 H, NH). ^{13}C NMR [75 MHz, $(CD_3)_2SO$]: δ 17.4 (Me), 61.3 (CH_2), 123.5, 124.0 (CH of C_6H_4), 127.6 (C of C_6H_4), 128.7, 129.0 (C of Xy), 129.1 (CH of C_6H_4), 132.0 (*ipso*-C of Xy), 133.8 (CH of C_6H_4), 135.3 (C of Xy), 144.6 (CH of C_6H_4), 161.1 (s, CN). Anal. Calcd for $C_{17}H_{17}F_3N_2O_3S$: C, 52.84; H, 4.43; N, 7.25; S, 8.30. Found: C, 53.04; H, 4.64; N, 7.39; S, 7.86. FAB$^+$-MS: *m*/*z* 237 [M$^+$].

Synthesis of [2-(XyNH)-4-OMe-isoindolinium]OTf (9b·OTf). 9b·OTf was obtained starting from **1b** (119 mg, 0.184 mmol), XyNC (49 mg, 0.374 mmol), and TlOTf (0.371 mmol). Yield: 60 mg, 39%. Mp: 198 °C. IR (Nujol, cm^{-1}): ν 1660 (C=N). ^{1}H NMR [300 MHz, $(CD_3)_2SO$]: δ 2.24 (s, 6 H, Me), 3.90 (s, 3 H, OMe), 4.75 (s, 2 H, CH_2), 7.29−7.38 (m, 3 H, C_6H_3), 7.45 (dd, 1 H, H5, ^3J(H,H) = 8.4, ^4J(H,H) = 2.6 Hz), 7.71 (d, 1 H, H6, ^3J(H,H) = 8.4 Hz), 7.97 (d, 1 H, H3, ^4J(H,H) = 2.6 Hz), 10.39 (s, 1 H, NH), 11.47 (s, 1 H, NH). ^{13}C NMR 75 MHz, $(CD_3)_2SO$]: δ 17.4 (Me), 51.1 (CH_2), 55.8 (OMe), 106.9, 121.6, 125.0 (CH of C_6H_3), 128.7 (C of C_6H_3), 129.0, 129.1 (C of Xy), 131.8 (*ipso*-C of Xy), 135.3 (C of Xy), 136.8 (C of C_6H_3), 159.7 (COMe), 161 (CN). Anal. Calcd for $C_{18}H_{19}F_3N_2O_4S$: C, 51.92; H, 4.60; N, 6.73; S, 7.70. Found: C, 52.14; H, 4,94; N, 6.87; S, 7.53. FAB$^+$-MS: *m*/*z* 267.3 [M$^+$].

Synthesis of [2-(XyNH)-4-F-isoindolinium]OTf (9d·OTf). 9d·OTf was obtained starting from **1d** (121 mg, 0.195 mmol), XyNC (51 mg, 0.389 mmol), and TlOTf (138 mg, 0.390 mmol). Yield: 40 mg, 25%. Mp: 165 °C. IR (Nujol, cm^{-1}): ν 1658 (C=N). ^{1}H NMR [300 MHz, $(CD_3)_2SO$]: δ 2.24 (s, 6 H, Me), 4.83 (s, 2 H, CH_2), 7.28−7.38 (m, 3 H, Xy), 7.75 (td, 1 H, H5, ^3J(F,H) = ^3J(H,H) = 8.9 Hz, ^4J(H,H) = 2.4 Hz), 7.87 (dd, 1 H, H6, ^3J(H,H) = 8.6 Hz, ^4J(F,H) = 4.7 Hz), 8.19 (dd, 1 H, H3, ^3J(F,H) = 8.3 Hz, ^4J(H,H) = 2.4 Hz), 10.59 (s, 1 H, NH), 11.56 (s, 1 H, NH). ^{13}C NMR [75 MHz, $(CD_3)_2SO$]: δ 17.4 (Me), 51.4 (CH_2), 110.2 (d, C(3) or C(5), ^2J(C,F) = 25.6 Hz), 121.5 (d, C(3) or C(5), ^2J(C,F) = 23.2 Hz), 126.2 (d, C(6), ^3J(C,F) = 9.1 Hz), 129.0 (CH of Xy), 129.2 (CH of Xy), 129.3 (d, C(9), ^3J(C,F) = 10.4 Hz), 131.7 (*ipso*-C of Xy), 135.3 (C of Xy), 140.8 (d, *p*-C of C_6H_3F, ^4J(C,F) = 1.8 Hz), 160.4 (d, *C*NXy, ^4J(C,F) = 3.6 Hz), 161.9 (d, C(4), ^1J(C,F) = 244.8 Hz). Anal. Calcd for $C_{17}H_{16}F_4N_2O_3S$: C, 50.49; H, 3.99; N, 6.93; S, 7.93. Found: C, 50.45; H, 4,08; N, 7.04; S, 7.49. FAB$^+$-MS: *m*/*z* 255.3 [M$^+$].

Synthesis of [2-(^{t}BuNH)-isoindolinium]OTf (10a·OTf). 10a·OTf was obtained starting from **1a** (120 mg, 0.205 mmol), ^{t}BuNC (46 μL, 0.407 mmol), and TlOTf (145 mg, 0.410 mmol). Yield: 69 mg, 50%. Mp: 201 °C. IR (Nujol, cm^{-1}): ν 1660 (C=N). ^{1}H NMR [200 MHz, $(CD_3)_2CO$]: δ 1.64 (s, 9 H, Me), 5.03 (s, 2 H, CH_2), 7.59−7.67 (m, 2 H, C_6H_4), 7.80−7.82 (m, 1 H, C_6H_4), 8.31−8.35 (m, 1 H, C_6H_4), 8.85 (s, 1 H, NH), 9.50 (s, 1 H, NH). ^{13}C NMR [50 MHz, $(CD_3)_2CO$]: δ 28.0 (Me), 53.2 (CH_2), 55.1 (*C*Me_3), 124.1, 124.2, 129.1, 134.2 (CH), 143.8, 160.9 (C of C_6H_4), 166.2 (*C*N^{t}Bu). Anal. Calcd for $C_{13}H_{17}F_3N_2O_3S$: C, 46.15; H, 5.06; N, 8.28; S, 9.48. Found: C, 46.12; H, 5.32; N, 8.33; S, 9.19. FAB$^+$-MS: *m*/*z* 189.3 [M$^+$].

Synthesis of [2-(^{t}BuNH)-4-OMe-isoindolinium]OTf (10b·OTf). 10b·OTf was obtained starting from **1b** (126 mg, 0.195 mmol), ^{t}BuNC (44 μL, 0.390 mmol), and TlOTf (138 mg, 0.390 mmol). Yield: 65 mg, 45%. Mp: 217 °C. IR (Nujol, cm^{-1}): ν 1656 (C=N). ^{1}H NMR [300 MHz, $(CD_3)_2CO$]: δ 1.63 (s, 9 H, Me), 3.87 (s, 3 H, OMe), 4.93 (s, 2 H, CH_2), 7.34 (dd, 1 H, H5, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.3 Hz), 7.68 (d, 1 H, H6, ^3J(H,H) = 8.5 Hz), 7.91 (d, 1 H, H3, ^4J(H,H) = 2.3 Hz), 8.80 (s, 1 H, NH), 9.46 (s, 1 H, NH). ^{13}C NMR [75 MHz, $(CD_3)_2CO$]: δ 28.4 (Me), 53.1 (CH_2), 55.5 (*C*Me_3), 56.5 (OMe), 107.3, 123.0, 125.4 (CH), 131.3, 136.4 (C of C_6H_3OMe), 161.3 (*C*N^{t}Bu), 161.4 (COMe). Anal. Calcd for $C_{14}H_{19}F_3N_2O_4S$: C, 45.65; H, 5.20; N, 7.60; S, 8.70. Found: C, 45.50; H, 5.56; N, 7.74; S, 8.47. FAB$^+$-MS: *m*/*z* 219.3 [M$^+$].

Synthesis of [2-(^{t}BuNH)-4-F-isoindolinium]OTf (10d·OTf). 10d·OTf was obtained starting from **1d** (109 mg, 0.176 mmol), ^{t}BuNC (40 μL, 0.354 mmol), and TlOTf (125 mg, 0.354 mmol). Yield: 65 mg, 52%. Mp: 174 °C. IR (Nujol, cm^{-1}): ν 1659 (C=N). ^{1}H NMR [300 MHz, $(CD_3)_2CO$]: δ 1.64 (s, 9 H, Me), 5.02 (s, 2 H, CH_2), 7.60 (td, 1 H, H5, ^3J(H,H) = ^3J(F,H) = 8,9 Hz, ^4J(H,H) = 2.4 Hz), 7.87 (dd, 1 H, H6, ^3J(H,H) = 8.4 Hz, ^4J(F,H) = 4.7 Hz), 8.19 (dd, 1 H, H3, ^3J(F,H) = 8.6 Hz, ^4J(H,H) = 2.3 Hz), 8.89 (s, 1 H, NH), 9.63 (s, 1 H, NH). ^{13}C NMR [75 MHz, $(CD_3)_2CO$]: δ 28.3 (Me), 53.3 (CH_2), 55.7 (*C*Me_3), 111.4 (d, C(3) or C(5), ^2J(C,F) = 25.6 Hz), 122.0 (d, C(3) or C(5), ^2J(C,F) = 23.8 Hz), 126.5 (d, C(6), ^3J(C,F) = 8.5 Hz), 131.8 (d, C of C_6H_3F, ^3J(C,F) = 10.4 Hz), 140.0 (C of C_6H_3F), 160.6 (*C*N^{t}Bu), 163.5 (d, C(9), ^1J(C,F) = 246.0 Hz). Anal. Calcd for $C_{13}H_{16}F_4N_2O_3S$: C, 43.82; H, 4.53; N, 7.86; S, 9.00. Found: C, 44.11; H, 4.66; N, 7.93; S, 8.75. FAB$^+$-MS: *m*/*z* 207.3 [M$^+$].

Synthesis of [Pd{C(=NXy)$C_6H_4CH_2NH_2$-2}Br]$_2$ (11). A suspension of **2a** (84 mg, 0.198 mmol) in toluene (10 mL) was refluxed for 6 h. Filtration of the reaction mixture and washing the solid with CH_2Cl_2 gave **11** as an olive green solid. Due to the insolubility in common organic solvents, no NMR data are available. Yield: 50 mg, 60%. Dec pt: 226 °C. IR (Nujol, cm^{-1}): ν 1576, 1538 (C=N). Anal. Calcd for $C_{32}H_{34}Br_2N_4Pd_2$: C, 45.26; H, 4.04; N, 6.60. Found: C, 45.04; H, 3.83; N, 6.43.

Synthesis of [$PdBr_2${2-(XyNH)-isoindole}$_2$] (12). XyNC (48 mg, 0.366 mmol) was added to a suspension of **1a** (85 mg, 0.145 mmol) in 10 mL of toluene. On refluxing the reaction mixture for 3 h, Pd(0) was precipitated. The solution was removed in vacuo, and the remaining black residue was extracted with CH_2Cl_2. The CH_2Cl_2 extract was filtered through $MgSO_4$. On concentrating the yellow filtrate to about

Table 2. Crystal Data for Complexes 3d, 9a·OTf, and 12

	3d	**9a**·OTf	**12**
formula	$C_{12}H_{16}BrFN_2Pd$	$C_{17}H_{17}F_3N_2O_3S$	$C_{32}H_{32}Br_2N_4Pd$
M_r	393.58	386.39	738.84
cryst size (mm)	0.44 × 0.44 × 0.34	0.40 × 0.25 × 0.18	0.52 × 0.18 × 0.14
cryst syst	triclinic	monoclinic	triclinic
cell constants			
a (Å)	5.3580(3)	10.5482(12)	7.9207(7)
b (Å)	10.0813(6)	11.9641(14)	8.9482(8)
c (Å)	13.6049(8)	13.9946(16)	11.1669(8)
α (deg)	80.825(5)	90	95.579(7)
β (deg)	82.462(4)	100.052(3)	100.911(5)
γ (deg)	76.751(4)	90	99.556(7)
V (Å^3)	702.73(7)	1739.0(3)	759.58(11)
Z	2	4	1
λ (Å)	0.71073	0.71073	0.71073
T (K)	173(2)	143(2)	173(2)
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
ρ_{calc} (Mg/m^3)	1.860	1.476	1.615
abs coeff (mm^{-1})	4.155	0.237	3.268
transmn	0.914/0.654		0.902/0.762
F(000)	384	800	368
θ range (deg)	3.05−25.00	2.24−30.03	3.18−27.50
limiting indices	$-6 \le h \le 6$	$-14 \le h \le 14$	$-10 \le h \le 10$
	$-11 \le k \le 11$	$-16 \le k \le 8$	$-11 \le k \le 11$
	$-16 \le l \le 1$	$-19 \le l \le 18$	$-14 \le l \le 14$
no. of reflns			
measd	2626	14 177	6477
indep	2473	5073	3493
R_{int}	0.0088	0.0567	0.0147
abs corr	*ψ* scans	none	*ψ* scans
no. of data/restraints/params	2473/9/166	5073/0/245	3493/179/181
R1[a]	0.0213	0.0390	0.0266
wR2[b]	0.0500	0.0967	0.0685
largest diff peak (e Å^{-3})	0.415	0.362	0.562
$S(F^2)$[c]	1.061	0.927	1.161

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$ for reflections with $I > 2\sigma(I)$. [b] $wR2 = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and *a* and *b* are constants adjusted by the program. [c] $S(F^2) = [\sum\{w(F_o^2 - F_c^2)^2\}/(n - p)]^{0.5}$, where *n* is the number of data and *p* the number of parameters.

1 mL of volume and adding hexane, a yellow solid precipitated, which was filtrated off, washed with hexane, and dried in vacuo. Yield: 24 mg, 45%. Dec pt: 140 °C. IR (Nujol, cm^{-1}): *ν* 1620 (C═N). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 2.37 (s, 12 H, Me), 4.88 (s, 4 H, CH_2), 6.24−7.47 (m, 7 H, C_6H_4 and C_6H_3), 8.05 (br s, 2 H, NH). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 19.1 (Me), 60.4 (CH_2), 121.2, 122.1, 127.0, 128.2, 128.5, 129.6 (CH of C_6H_4 and C_6H_3), 131.6, 135.1, 137.8, 150.1 (C of C_6H_4, C_6H_3), 164.1 (C═N). Anal. Calcd for $C_{32}H_{34}Br_2N_4Pd$: C, 52.02; H, 4.37; N, 7.58. Found: C, 51.93; H, 4.32; N, 7.38.

X-ray Structure Determinations. X-ray intensities of compound **3d** and **12** were measured on a Siemens P4 with a LT2 low-temperature attachment. Compound **9a·OTf** was measured on a Bruker SMART 1000 CCD/LT3. See Table 2. The structures of the compounds **3d** and **9a·OTf** were solved by direct methods, compound **12** was solved by the heavy atom method, and all were refined anisotropically on F^2 (compounds **12** and **9a·OTf**, program SHELX-97; **3d**, program SHELX-93, G. M. Sheldrick, University of Göttingen). The hydrogens at N were located in the Fourier difference maps and refined freely. Methyl groups were refined using rigid groups, for the compounds **3d** and **9a·OTf**; in the latter, the methyl hydrogens at C(15) are disordered over two positions. Other hydrogens were refined using a riding method.

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Supporting Information Available: Listing of all refined and calculated atomic coordinates, all anisotropic thermal parameters, and all bond lengths and angles for complexes **3d**, **9a·OTf**, and **12**. The method of synthesis of $IC_6H_4CH_2NH_2$-2 and ($IC_6H_4CH_2NH_3$-2)OTf. This material is available free of charge via the Internet at http://pubs.acs.org.

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