Synthesis and Reactivity toward Isonitriles of (2-Aminoaryl)palladium(II) Complexes

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Received June 11, 2001

Mixtures of "$Pd(dba)_2$" (dba = dibenzylideneacetone) and 2,2′-bipyridine (bpy; 1:2) or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda; 1:1) react with 2-bromo-4-nitroaniline to give [Pd{$C_6H_3NH_2$-2-NO_2-5}Br(N−N)] (N−N = bpy (**1b**), tmeda (**1b′**)). Reactions of 2-iodoaniline with mixtures of "$Pd(dba)_2$" and isonitriles RNC (R = $C_6H_3Me_2$-2,6 (Xy), 2:1:2 molar ratios; R = ^{t}Bu, 2.9:1:2 molar ratios) result in the formation of the complexes [Pd{κ^2C,N-C(=NXy)-$C_6H_4NH_2$-2}I(CNXy)] (**2a**) and *trans*-[Pd{C(=N^{t}Bu)$C_6H_4NH_2$-2}I(CN^{t}Bu)$_2$] (**3a***). The reactions of [Pd{$C_6H_4NH_2$-2}I(bpy)] and **1b′** with RNC give the complexes *trans*-[Pd{C(=NR)$C_6H_3NH_2$-2-Y-5}}X(CNR)$_2$] (Y = H, X = I, R = Xy (**3a**), ^{t}Bu (**3a***); Y = NO_2, X = Br, R = Xy (**3b**), ^{t}Bu (**3b***)). Complexes **3** react with Tl(TfO) (TfO = CF_3SO_3) to give decomposition products, with the exception of **3a**, which gives the cyclopalladated complex *cis*-[Pd{κ^2C,N-C(=NXy)$C_6H_4NH_2$-2}(CNXy)$_2$]TfO (**4a**). Complex **2a** or **3** reacts with Tl(TfO) in the presence of the corresponding ligand, L or L_2, to give the cationic complex [Pd{C(=NR)$C_6H_3NH_2$-2-Y-5}(CNR)L_2]TfO (L = ^{t}BuNC, Y = H (**5a***), NO_2 (**5b***); L_2 = bpy, Y = H, R = Xy (**6a**), ^{t}Bu (**6a***)). When L = PPh_3, the resulting complexes *trans*-[Pd{C(=NR)$C_6H_3NH_2$-2-Y-5}(CN-^{t}Bu)$_2$(PPh_3)]TfO (Y = H (**7a***), NO_2 (**7b***)) decompose easily to the Pd(I) complex [Pd_2(CN-^{t}Bu)$_4$(PPh_3)$_2$](TfO)$_2$ (**8**). The reaction of **2a** with Tl(TfO) affords [{Pd[κ^2C,N-C(=NXy)C_6H_4-NH_2](CNXy)}$_2$(μ-I)]TfO (**9a**), and that with a mixture of bpy and Tl(TfO) in acetone with subsequent bubbling of CO through the solution gives [Pd(R)(CNXy)(bpy)](TfO)$_2$ (**10**), where R is 2-(xylylamino)-3-xylylquinazolinium-4-yl. The crystal structures of **2a**, **3a**, **4a**, **6a**, **8**, **9a**·CH_2Cl_2, and **10**·1.5CH_2Cl_2 have been determined by X-ray diffraction studies. Some hydrogen bond interactions (C_{sp^3}−H···Pd, N−H···π−arene, N−H···I−Pd; eight-membered rings ···O−S−O···H−N−C−C−H··· and ···I−Pd−N−H···I−Pd−N−H···) lead to interesting supramolecular structures.

Introduction

Arylpalladium complexes participate in many palladium-catalyzed organic reactions involving carbon−carbon[1−3] or carbon−heteroatom bond formation: for example, the formation of carbon−nitrogen,[3−5] carbon−oxygen,[6] or carbon−phosphorus bonds.[7] In particular, (2-aminophenyl)palladium species are intermediates in the palladium-catalyzed formation of nitrogen-containing heterocycles from *o*-iodo- or *o*-bromoanilines and, for example, alkynes,[8] dienes,[9,10] and vinyl cyclopropanes

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10.1021/om0104971 CCC: $22.00
Publication on Web 12/20/2001

and cyclobutanes,[11] as well as in intramolecular cascade cyclizations.[12] The palladium-catalyzed synthesis of 2-aryl- and 2-vinyl-4*H*-3,1-benzoxazin-4-ones from 2-iodoaniline, carbon monoxide, and the appropriate organic halides or triflates has been reported.[13] A palladium-catalyzed domino process to give 1-benzazepines from 2-iodoaniline and homoallylic alcohols has also been developed.[14] These results have encouraged us to isolate (2-aminoaryl)palladium complexes and to study their reactivity. We have reported previously the synthesis of (2-amino-5-nitrophenyl)palladium complexes via oxidative addition of the corresponding bromoarene to $[Pd(PPh_3)_4]$.[15] More recently we have prepared (2-aminophenyl)palladium complexes by the oxidative addition of 2-iodoaniline to Pd(0) species and studied their reactivity toward carbon monoxide and oxygen.[16,17] In this context, we wish to report here on the synthesis of new (2-aminoaryl)palladium complexes and a study of their reactivity with isonitriles.

Isonitriles usually react with organopalladium complexes to give imidoyl compounds. Such insertion reactions have been observed with alkyl-,[18−31] alkynyl-,[28,32−35] aryl-,[36−48] and other[49−53] organopalladium complexes. Moreover, di-,[20,25,26,32,33,42,54] tri-,[20,55] and polyinsertion reactions, which are relevant in the palladium-mediated, screw-sense-selective polymerization of isonitriles, have been reported.[54,56,57] In some cases, these insertions can be followed by a transformation of the resultant ligand to give, for example, a σ-bonded vinylketenimine,[50] a coordinated β-keto imino fragment,[25] or, after a depalladation process, organic compounds.[24−26,36,38−41,58] We have reported the synthesis of a highly functionalized ketenimine by the reaction of a (2,3,4-trimethoxy-6-formylphenyl)palladium complex with 2,6-dimethylphenyl isocyanide.[43] The imidoyl complexes reported have been prepared (i) by reacting isonitriles with alkyl,[19,20,23,25,27−30,39,55,59] aryl,[20,30,35,37,38,40,42−44,55] alkynyl,[28,32,33,56] or other organopalladium complexes,[49,51,52,59] (ii) via transmetalation reactions involving an organosodium[52] or an organomercury compound[60] and a palladium isonitrile complex, and (iii) by the thermal rearrangement of an organo(isonitrile)palladium complex.[46,47,61] In this paper, we report the synthesis of imidoyl complexes involving (i) insertion reactions of isonitriles with (2-aminoaryl)palladium complexes or (ii) oxidative addition reactions of 2-iodoaniline or 2-bromo-4-nitroaniline with $Pd(CNR)_2$ (R = Xy = 2,6-dimethylphenyl, ^{t}Bu). This method has only been used with a few alkylpalladium complexes, and the results were different from those we

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report here.[59] We have recently used the same method of synthesis starting from 2-ROC_6H_4I (R = H, C(O)-Me).[62]

Experimental Section

C, H, N, and S analyses, melting point measurements, infrared and NMR spectra, and purification of solvents were carried out as described previously.[63] The complex "Pd(dba)$_2$" ([$Pd_2(dba)_3$]·dba; dba = dibenzylideneacetone) was prepared by following described procedures.[1,64] The compound [Pd{C_6H_4-NH_2-2}I(bpy)] (**1a**) was prepared as reported previously.[17] Preparative TLC separations were carried out on silica 60 AC.C 70−200 μm.

Synthesis of [Pd{$C_6H_3NH_2$-2-NO_2-5}Br(bpy)] (1b). "Pd-(dba)$_2$" (160 mg, 0.28 mmol) and bpy (2,2′-bipyridine) (87 mg, 0.55 mmol) were mixed in toluene (10 mL) under nitrogen and stirred for 15 min. 2-Bromo-4-nitroaniline was then added and the resulting mixture stirred at 130 °C in a silicone oil bath for a few minutes until the red color disappeared. The hot bath was then substituted by a cooled water bath, and solvents were removed in vacuo. The residue was extracted with acetone (15 cm^3), and the extracts were filtered through anhydrous magnesium sulfate. The magnesium sulfate was washed with hot acetone (3 × 5 cm^3), and the washing liquors were added to the extracts. The resulting solution was evaporated almost to dryness. Addition of Et_2O precipitated a yellow solid which was washed with Et_2O and dried in a current of air, giving yellow **1b**. Yield: 65 mg, 50%. IR (Nujol, cm^{-1}): ν 3438 (NH), 3326 (NH). ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ 9.16 (d, $^4J_{H,H}$ = 4 Hz, 1 H, H6), 8.12 (d, $J_{H,H}$ = 2 Hz, 2 H, bpy), 8.27 (m, 2 H, bpy), 7.88−7.45 (several m, 6 H, bpy and aryl), 6.4 (b s, 2 H NH_2). Compound **1b** could not be isolated as an analytically pure compound (see Discussion).

Synthesis of [Pd{$C_6H_3NH_2$-2-NO_2-5}Br(tmeda)] (1b′). "Pd(dba)$_2$" (200 mg, 0.34 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda; 40 mg, 0.34 mmol) were mixed in toluene (10 mL) under nitrogen, and the mixture was stirred for 15 min. 2-Bromo-4-nitroaniline (150 mg, 0.69 mmol) was then added, and the mixture was heated slowly until its color turned from red to orange-yellow. The solvent was removed in vacuo and the residue treated with CH_2Cl_2 (12 cm^3) and filtered through Celite. The resulting yellow solution was evaporated to dryness and Et_2O added to precipitate the compound, which was filtered, washed with Et_2O and *n*-hexane, and air-dried. This solid was purified by preparative TLC with CH_2Cl_2/Et_2O (3:1), R_f = 0.46. Yield: 92 mg, 60%. Mp: 192 °C. IR (Nujol, cm^{-1}): ν 3440 (NH), 3316 (NH). ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ 7.87 (d, $^4J_{H,H}$ = 2.5 Hz, 1 H, H6), 7.59 (dd, $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,H}$ = 2.5 Hz, 1 H, H4), 6.30 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, H3), 5.76 (b s, 2 H NH_2), 3.15−2.5 (several m, 4H, CH_2), 2.69 (s, 3 H, Me), 2.67 (s, 3 H, Me), 2.60 (s, 3 H, Me), 2.47 (s, 3 H, Me). Anal. Calcd for $C_{12}H_{21}BrN_4O_2Pd$: C, 32.78; H, 4.81; N, 12.74. Found: C, 33.23; H, 4.66; N, 12.51.

Synthesis of [Pd{κ^2*C*,*N*-C(=NXy)$C_6H_4NH_2$-2}I(CNXy)] (2a). Pd(dba)$_2$ (400 mg, 0.70 mmol) and XyNC (Xy = C_6H_3-Me_2-2,6; 184 mg, 1.40 mmol) were mixed in toluene (60 mL) at −5 °C and stirred for 5 min under N_2. Then, $C_6H_4NH_2$I-2 (302 mg, 1.40 mmol) was added and the temperature of the reaction mixture maintained for a further 4 h. The reaction mixture was stirred for 3 days more at room temperature. The resulting suspension was then evaporated to dryness, the residue was extracted with CH_2Cl_2, and the extracts were filtered through anhydrous $MgSO_4$. The green-brown solution was concentrated and Et_2O added to precipitate **2a** as a pale yellow-green solid. Yield: 275 mg, 65%. Dec pt: 160 °C. IR (Nujol, cm^{-1}): ν 3166 (NH), 3140 (NH), 2170 (C≡N), 1640 (N=C). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.16 (d, $J_{H,H}$ = 11 Hz, 1 H), 7.5−7.0 (several m, aromatics, 4 H), 6.96 (d, $J_{H,H}$ = 11 Hz, 2 H), 6.75 (d, $J_{H,H}$ = 11 Hz, 2 H), 6.27 (t, $J_{H,H}$ = 11 Hz, 1 H), 5.44 (s, NH_2, 2 H), 2.24 (s, 2Me, 6H), 2.21 (s, 2Me, 6H). ^{13}C-{^{1}H} NMR (50 MHz, $CDCl_3$): δ 175.0 (C=N), 152.2 (CN), 144.1, 142.9, 134.0, 131.7 (C−H), 128.8 (C−H), 128.2 (C−H), 127.5 (C−H), 127.4 (C−H), 127.0, 126.8 (C−H), 124.6 (C−H), 123.7 (C−H), 19.2 (Me), 18.6 (Me). Anal. Calcd for $C_{24}H_{24}IN_3Pd$: C, 49.04; H, 4.12; N, 7.15. Found: C, 49.33; H, 4.06; N, 7.18. Single crystals of **2a** were grown by slow diffusion of *n*-hexane into solutions of **2a** in CH_2Cl_2.

Synthesis of *trans*-[Pd{C(=N^{t}Bu)$C_6H_4NH_2$-2}I(CN-^{t}Bu)$_2$] (3a*). Method A. "Pd(dba)$_2$" (360 mg, 0.63 mmol) and ^{t}BuNC (138 μL, 1.3 mmol) were mixed in toluene (30 mL) at 0 °C under nitrogen and stirred for 5 min. 2-Iodoaniline (390 mg, 1.8 mmol) was then added, and the mixture was warmed slowly to room temperature and stirred for a further 15 h. The solvent was evaporated in vacuo, CH_2Cl_2 (20 mL) was added, and the resulting suspension was filtered through Celite. The yellow solution was evaporated to dryness, the residue was washed with Et_2O and filtered, and the solid was washed with Et_2O and *n*-hexane and air-dried, giving **3a*** as a yellow solid. Yield: 210 mg, 81% with respect to isonitrile.

Method B. ^{t}BuNC (42 μL, 0.37 mmol) was added to a solution of **1a** (60 mg, 0.12 mmol) in CH_2Cl_2 (10 mL) at room temperature. The pale yellow solution was stirred for 10 min and the solvent evaporated to dryness. Addition of *n*-hexane (10 mL) precipitated a solid which was filtered, washed with *n*-hexane, and air-dried to give **3a***. Yield: 51 mg, 70%. Mp: 149 °C. IR (Nujol, cm^{-1}): ν 3403 (NH), 3203 (NH), 2187 (C≡N). ^{1} H NMR (300 MHz, $CDCl_3$): δ 8.46 (dd, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 1.5 Hz, 1 H, H6), 7.01 (ddd, $^3J_{H,H}$ = 8 Hz, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 1.5 Hz, 1 H, H4 or H5), 6.72 (ddd, $^3J_{H,H}$ = 8 Hz, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 1.5 Hz, 1 H, H4 or H5), 6.56 (dd, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 1.5 Hz, 1 H, H3), 6.02 (s, 2H NH_2), 1.62 (s, 9 H, 3Me), 1.37 (s, 18 H, 6Me). Anal. Calcd for $C_{21}H_{33}IN_4OPd$: C, 43.88; H, 5.79; N, 9.75. Found: C, 44.20; H, 5.67; N, 9.57.

Synthesis of *trans*-[Pd{C(=N^{t}Bu)$C_6H_4NH_2$-2}I(CNXy)$_2$] (3a). XyNC (67 mg, 0.51 mmol) was added to a solution of **2a** (300 mg, 0.51 mmol) in CH_2Cl_2 (15 mL) at 0 °C, and the resulting suspension was warmed slowly to room temperature and stirred overnight. The solvent was removed in vacuo and Et_2O added to give **3a** as a pale yellow solid. Yield: 293 mg, 80%. Dec pt: 140 °C. IR (Nujol, cm^{-1}): ν 3450 (NH), 3374 (NH), 3290 (NH), 2180 (C≡N). ^{1} H NMR (300 MHz, $CDCl_3$, −60 °C): δ 8.76 (d, $^3J_{H,H}$ = 8 Hz, 1 H, H6 *ortho* to imine group), 7.4−6.9 (several m, 10 H, Xy and H4 or H5, 6.85 (t, $^3J_{H,H}$ = 8 Hz, 1 H, H5 or H4), 6.72 (d, $^3J_{H,H}$ = 8 Hz, 1 H, H3), 6.3 (vb s, 2 H, NH_2), 2.23 (s, 12 H, Me), 2.16 (s, 6 H, Me). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, room temperature): δ 179.15 (C), 149.10 (C), 145.63 (C), 144.01 (b C), 138.06 (b, CH), 135.87 (C), 135.70 (C), 130.40 (CH), 129.89 (CH), 128.07 (CH), 127.96 (CH), 127.00 (C), 125.59 (b, C), 123.51 (CH), 116.05 (b, C−H), 115.32 (b, C−H), 19.04 (s, Me), 18.64 (s, Me). Anal. Calcd for $C_{33}H_{33}IN_4Pd$: C, 55.13; H, 4.63; N, 7.79. Found: C, 55.39; H, 4.51; N, 7.87. Single crystals of **3a** were grown by slow diffusion of *n*-hexane into solutions of **3a** in CH_2Cl_2.

Synthesis of *trans*-[Pd{C(=NXy)$C_6H_3NH_2$-2-NO_2-5}Br-(CNXy)$_2$] (3b). Method A. Complex **1b** (60 mg, approximately 0.13 mmol) was reacted with XyNC (70 mg, 0.38 mmol) in acetone (15 mL) for 10 min. The solvent was evaporated in vacuo and Et_2O (10 mL) added, causing the precipitation of a solid which was filtered, washed with Et_2O and *n*-hexane, and air-dried to give yellow **3b**. Yield: 68 mg, 75%.

Method B. 3b was similarly prepared from complex **1b′** (60 mg, 0.14 mmol) and XyNC (54 mg, 0.41 mmol). Yield: 85 mg, 87%. Mp: 160 °C. IR (Nujol, cm^{-1}): ν 3346 (NH), 2184 (C≡N). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.62 (d, $^4J_{H,H}$ = 3 Hz, 1 H, H6), 8.06 (dd, $^3J_{H,H}$ = 9 Hz, $^4J_{H,H}$ = 3 Hz, 1 H, H4), 7.3 (vb s,

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2 H, NH_2), 7.28−6.9 (several m, 9 H, XyNC), 6.67 (d, $^3J_{H,H}$ = 9 Hz, 1 H, H3), 2.24 (s, 12 H, 4Me), 2.16 (s, 6 H, 2Me). Anal. Calcd for $C_{33}H_{32}BrN_5O_2Pd$: C, 55.28; H, 4.50; N, 9.77. Found: C, 54.94; H, 4.39; N, 9.54.

Synthesis of *trans*-[Pd{C(=N^{t}Bu)$C_6H_3NH_2$-2-NO_2-5}Br-(CN^{t}Bu)$_2$] (3b*). This yellow complex was similarly prepared from **1b** (60 mg, approximately 0.13 mmol) and ^{t}BuNC (42 μL, 0.38 mmol) (method A) or from **1b′** (60 mg, 0.14 mmol) and ^{t}BuNC (46 μL, 0.41 mmol) (method B). Yield: 53 mg, 74% and 66 mg, 84%, respectively. Mp: 156 °C. IR (Nujol, cm^{-1}): ν 3336 (NH), 2192 (C≡N). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.22 (d, $^4J_{H,H}$ = 3 Hz, 1 H, H6), 7.92 (dd, $^3J_{H,H}$ = 9 Hz,$^4J_{H,H}$ = 3 Hz, 1 H, H4), 6.87 (s, 2 H, NH_2), 6.53 (d, $^3J_{H,H}$ = 9 Hz, 1 H, H3), 1.62 (s, 9 H, 3Me), 1.39 (s, 18 H, 6Me). Anal. Calcd for $C_{21}H_{32}BrN_5O_2Pd$: C, 44.03; H, 5.63; N, 12.23 found: C, 44.05; H, 5.94; N, 11.99.

Synthesis of *cis*-[Pd{κ^2*C,N*-C(=NXy)$C_6H_4NH_2$-2}(CNXy)$_2$]-TfO (4a). Tl(TfO) (100 mg, 0.28 mmol) was added to a solution of **3a** (200 mg, 0.28 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The resulting suspension was warmed slowly to room temperature and stirred overnight. The mixture was filtered through $MgSO_4$, the solvent removed in vacuo, and *n*-hexane added to precipitate **4a** as an orange solid. Yield: 151 mg, 73%. Dec pt: 105 °C. IR (Nujol, cm^{-1}): ν 3426 (NH), 3372 (NH), 3305 (NH), 2178 (C≡N). Λ_M = 144 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H, *ortho* to imine group), 7.75 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H, ortho to NH_2 group), 7.44 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, H4 or H5), 7.36−7.12 (m, 3 H, 3H4 of Xy), 7.05 (d, $^3J_{H,H}$ = 8 Hz, 4 H, 2H3 of Xy), 6.78 (d, $^3J_{H,H}$ = 8 Hz, 2 H, H3 of Xy), 6.72 (b s, 2 H, NH_2), 6.33 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, H5 or H4), 2.29 (b s, 12 H, 4Me), 2.20 (s, 6 H, 2Me). At −50 °C the broad signal corresponding to 4Me changed to two singlets at 2.33 (2 Me) and 2.27 (2 Me) ppm. Anal. Calcd for $C_{34}H_{33}F_3N_4O_3PdS$: C, 55.10; H, 4.49; N, 7.56; S, 4.33. Found: C, 54.55; H, 4.56; N, 7.63; S, 4.14. Single crystals of **4a** were grown by slow diffusion of *n*-hexane into solutions of **4a** in CH_2Cl_2.

Synthesis of [Pd{C(=N^{t}Bu)$C_6H_4NH_2$-2}(CN^{t}Bu)$_3$]TfO (5a*). ^{t}BuNC (27 μL, 0.17 mmol) and Tl(TfO) (62 mg, 0.17 mmol) were added to a solution of **3a*** (100 mg, 0.17 mmol) in acetone (10 mL). The resulting suspension was stirred for 15 min and then filtered through Celite. The filtrate was evaporated to dryness and Et_2O (10 mL) added, giving a solid which was filtered, washed with Et_2O (3 × 3 mL) and *n*-hexane (3 × 3 mL), and air-dried to give **5a*** as a yellow solid. Yield: 80 mg, 68%. Mp: 110 °C. IR (Nujol, cm^{-1}): ν 3432 (NH), 3320 (NH), 2280 (C≡N). Λ_M = 142 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (dd, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 1 Hz, 1 H, H6), 7.06 (ddd, $^3J_{H,H}$ = 8 Hz, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 1 Hz, 1 H, H4 or H5), 6.74 (ddd, $^3J_{H,H}$ = 8 Hz, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 1 Hz, 1 H, H4 or H5), 6.62 (dd, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 1.5 Hz, 1 H, H3), 5.98 (s, 2H NH_2), 1.61 (s, 9 H, 3Me), 1.57 (s, 9 H, 3Me), 1.42 (s, 18 H, 6Me). Anal. Calcd for $C_{27}H_{32}F_3N_5O_3PdS$: C, 47.68; H, 6.62; N, 10.30; S, 4.71. Found: C, 47.73; H, 6.48; N, 10.43; S, 4.58.

Synthesis of [Pd{C(=N^{t}Bu)$C_6H_3NH_2$-2-NO_2-5}(CN-^{t}Bu)$_3$]TfO (5b*). The yellow complex **5b*** was similarly prepared from **3b*** (37 mg, 0.034 mmol), ^{t}BuNC (7.5 μL, 0.064 mmol), and Tl(TfO) (23 mg, 0.064 mmol). Yield: 41 mg, 84%. Mp: 135 °C. Λ_M = 137 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): ν 3342 (NH), 2210 (C≡N). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.90 (d, $^4J_{H,H}$ = 2.5 Hz, 1 H, H6), 7.94 (dd, $^3J_{H,H}$ = 9 Hz, $^4J_{H,H}$ = 2.5 Hz, 1 H, H4), 7.62 (s, 2 H, NH_2), 6.86 (d, $^3J_{H,H}$ = 9 Hz, 1 H, H3), 1.63 (s, 9 H, 3Me), 1.57 (s, 9 H, 3Me), 1.44 (s, 18 H, 6Me). Anal. Calcd for $C_{32}H_{51}F_3N_6O_5PdS$: C, 44.72; H, 5.69; N, 11.59; S, 4.42. Found: C, 44.75; H, 6.05; N, 11.34; S, 4.93.

Synthesis of [Pd{C(=NXy)$C_6H_4NH_2$-2-(CNXy)}(bpy)]-TfO (6a). Bpy (40 mg, 0.26 mmol) and Tl(TfO) (95 mg, 0.27 mmol) were added to a solution of **2a** (150 mg, 0.26 mmol) in CH_2Cl_2 (12 mL). The resulting suspension was stirred for 3 h and then filtered. The filtrate was evaporated to dryness and Et_2O added to precipitate **2a** as a pale yellow solid. Yield: 179 mg, 91%. Dec pt: 165 °C. IR (Nujol, cm^{-1}): ν 3452 (NH), 3340 (NH), 2194 (C≡N). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.69 (d, $J_{H,H}$ = 8 Hz, 1 H), 8.24 (m, 2 H), 7.6−6.7 (several m, 15 H), 6.35 (b s, 2 H, NH_2), 2.23 (s, 6 H, 2Me), 1.91 (s, 6 H, 2Me). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 179.04 (C=N), 154.79, 150.24 (C−H), 148.95, 147.05, 141.64 (b, C−H), 136.10 (C−H), 135.55 (CN), 131.58 (C−H), 130.83 (C−H), 128.48 (C−H), 128.33 (C−H), 127.48 (C−H), 126.71, 123.97 (C−H), 121.36, 117.64, 116.76 (C−H), 116.09 (C−H), 18.99 (Me), 18.62 (Me). ^{19}F NMR (282 MHz, $CDCl_3$): δ −77.8 (s, CF_3). Anal. Calcd for $C_{35}H_{32}F_3N_5O_3PdS$: C, 54.87; H, 4.21; N, 9.14; S, 4.18. Found: C, 54.34; H, 4.27; N, 8.76; S, 4.23. Single crystals of **6a** were grown by slow diffusion of *n*-hexane into solutions of **6a** in CH_2Cl_2.

Synthesis of [Pd{C(=N^{t}Bu)$C_6H_4NH_2$-2}(CN^{t}Bu)(bpy)]-TfO (6a*). bpy (34 mg, 0.19 mmol) and Tl(TfO) (68 mg, 0.21 mmol) were added to a solution of complex **3a*** (100 mg, 0.17 mmol) in acetone (10 mL). The resulting suspension was stirred for 15 min and then filtered through Celite. The filtrate was evaporated to dryness and the residue triturated with Et_2O (10 mL). The resulting solid was filtered, washed with Et_2O (3 × 3 mL), and air-dried to give **6a*** as a yellow solid. Yield: 100 mg, 86%. Mp: 132 °C. Λ_M = 135 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): ν 3370 (NH), 2212 (C≡N). ^{1} H NMR (300 MHz, $CDCl_3$): δ 8.7−6.5 (several m, 12 H), 6.89 (s, 2H, NH_2), 1.63 (s, 9 H, 3Me), 1.58 (s, 9 H, 3Me). Anal. Calcd for $C_{27}H_{42}F_3N_5O_3PdS$: C, 48.40; H, 4.81; N, 10.45; S, 4.79. Found: C, 48.63; H, 4.91; N, 10.60; S, 4.75.

Synthesis of *trans*-[Pd{C(=N^{t}Bu)$C_6H_4NH_2$-2}(CN^{t}Bu)$_2$-(PPh$_3$)]TfO (7a*). PPh_3 (45 mg, 0.16 mmol) and Tl(TfO) (61 mg, 0.16 mmol) were added to a solution of complex **3a*** (94 mg, 0.16 mmol) in acetone (15 mL). The resulting suspension was stirred for 15 min and then filtered through Celite. The filtrate was evaporated to dryness and the residue triturated with Et_2O (10 mL). The resulting solid was filtered, washed with Et_2O (33 mL) and *n*-hexane, and air-dried to give **7a*** as a yellow solid. Yield: 128 mg, 92%. IR (Nujol, cm^{-1}): ν 3394 (NH), 2198 (C≡N). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.49 (dd, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 1.5 Hz, 1 H, H6), 7.62−7.31 (m, 15 H, PPh_3), 7.09 (ddd, $^3J_{H,H}$ = 8 Hz, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 1.5 Hz, 1 H, H4 or H5), 6.76 (ddd, $^3J_{H,H}$ = 8 Hz, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 1.5 Hz, 1 H, H4 or H5), 6.67 (dd, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 1.5 Hz, 1 H, H3), 5.92 (s, 2 H NH_2), 1.60 (s, 9 H, 3Me), 1.13 (s, 18 H, 6Me). ^{31}P NMR (121 MHz, $CDCl_3$): δ 14.38 (s, PPh_3). These NMR spectra show small signals due to the presence of impurities, including **8** (see Discussion). These impurities could not be removed.

Synthesis of *trans*-[Pd{C(=N^{t}Bu)$C_6H_3NH_2$-2-NO_2-5}-(CN^{t}Bu)$_2$(PPh$_3$)]TfO (7b*). This yellow complex was similarly prepared from **3b*** (60 mg, 0.11 mmol), PPh_3 (28 mg, 0.11 mmol), and Tl(TfO) (37 mg, 0.11 mmol). Yield: 75 mg, 79%. IR (Nujol, cm^{-1}): ν 3392 (NH), 2208 (C≡N). ^{1} H NMR (200 MHz, $CDCl_3$): δ 9.15 (d, $^4J_{H,H}$ = 3 Hz, 1 H, H6), 7.95 (dd, $^3J_{H,H}$ = 9 Hz, $^4J_{H,H}$ = 3 Hz, 1 H, H4), 7.60−7.45 (m, 17 H, PPh_3 + NH_2), 6.93 (d, $^3J_{H,H}$ = 9 Hz, 1 H, H3), 1.64 (s, 9 H, 3Me), 1.11 (s, 18 H, 6Me). ^{31}P NMR (121 MHz, $CDCl_3$): δ 14.47 (s, PPh_3). These NMR spectra contain small signals due to the presence of impurities, including **8** (see Discussion). These impurities could not be removed.

Synthesis of [Pd$_2$(CN^{t}Bu)$_4$(PPh$_3$)$_2$](TfO)$_2$ (8). A sample of **7a*** or **7b*** was dissolved in the minimum amount of acetone or CH_2Cl_2. The solution was left standing for 24 h at room temperature. Et_2O was slowly added until a turbidity was observed; the mixture was left overnight in the refrigerator. In this way crystals of **8** were obtained, some of them suitable for X-ray determination studies. IR (Nujol, cm^{-1}): ν 2190 (C≡N). ^{1} H NMR (300 MHz, $CDCl_3$): δ 7.6−7.4 (m, 30 H, 2PPh_3), 1.30 (s, 36 H, 12Me), ^{31}P NMR (121 MHz, $CDCl_3$): δ 11.26 (s, PPh_3). Complex **8** was obtained in very small amounts and was analytically impure (see Discussion).

Table 1. Crystal Data for Complexes 2a, 3a, 4a, 6a, 8, 9a·CH_2Cl_2, and 10·1.5CH_2Cl_2

	2a	**3a**	**4a**	**6a**	**8**	**9a**·CH_2Cl_2	**10**·1.5CH_2Cl_2
formula	$C_{24}H_{24}IN_3Pd$	$C_{33}H_{33}IN_4Pd$	$C_{34}H_{33}F_3N_4O_3PdS$	$C_{35}H_{32}F_3N_5O_3PdS$	$C_{58}H_{66}F_6N_4O_6P_2Pd_2S_2$	$C_{50}H_{50}Cl_2F_3IN_6O_3Pd_2S$	$C_{46.5}H_{43}Cl_3F_6N_6O_6PdS_2$
M_r	587.76	718.93	741.10	766.12	1368.01	1282.62	1172.74
cryst size (mm)	0.62 × 0.42 × 0.38	0.60 × 0.25 × 0.15	0.60 × 0.25 × 0.20	0.64 × 0.24 × 0.18	0.25 × 0.09 × 0.09	0.56 × 0.44 × 0.40	0.58 × 0.38 × 0.34
cell constants							
a (Å)	15.937(3)	12.966(3)	12.3735(6)	8.127(1)	43.682(8)	14.3153(6)	11.671(2)
b (Å)	8.255(1)	12.378(3)	20.9499(13)	13.697(1)	14.327(3)	23.4738(9)	14.029(2)
c (Å)	17.410(3)	18.662(4)	13.3414(7)	15.975(1)	20.743(4)	15.8732(7)	18.294(3)
α (deg)	90	90	90	71.629(8)	90	90	100.938(14)
β (deg)	100.28(1)	90.28(3)	98.804(4)	81.22(1)	102.67(2)	105.903(3)	103.15(1)
γ (deg)	90	90	90	78.774(10)	90	90	111.112(10)
V (Å^3)	2253.7(6)	2995.2(12)	3417.7(3)	1647.4(3)	12665(4)	5129.8(4)	2596.4(7)
Z	4	4	4	2	8	4	2
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
T (K)	173(2)	143(2)	173(2)	173(2)	143(2)	173(2)	173(2)
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
monochromator	graphite	graphite	graphite	graphite	graphite	graphite	graphite
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$C2/c$	$P2_1/c$	$P\bar{1}$
μ (mm^{-1})	2.208	1.678	0.659	0.688	0.751	1.506	0.666
max/min transmissn (%)	0.487/0.341	0.862/0.720	0.879/0.693	0.8862/0.7998	0.862/0.356	0.5841/0.4860	0.805/0.699
abs cor	*ψ* scans	*ψ* scans	*ψ* scans	*ψ* scans	multiscan	*ψ* scans	*ψ* scans
diffractometer	Siemens P4	Stoe STADI-4	Siemens P4	Siemens P4	Bruker SMART	Siemens P4	Siemens P4
scan method	*ω*	*ω*/*θ*	*ω*	*ω*	*ω* and *ϕ*	*ω*	*ω*
2*θ* range (deg)	6 < 2*θ* < 50	6 < 2*θ* < 50	6 < 2*θ* < 50	6 < 2*θ* < 50	3.5 < 2*θ* < 53.7	6 < 2*θ* < 50	6 < 2*θ* < 50
hkl range	±*h*; ±*k*; +*l*	+*h*, −*k*, ±*l*	±*h*; −*k*; ±*l*	−*h*; ±*k*; ±*l*	sphere	±*h*; +*k*; −*l*	±*h*; +*k*; ±*l*
no. of rflns							
measd	6961	5516	9803	8397	69 459	10 733	9284
indep	3950	5280	5995	5723	12 946	8954	8881
R_{int}	0.035	0.0236	0.022	0.017	0.1586	0.018	0.017
R1[a]	0.0301	0.0323	0.0321	0.0369	0.0715	0.0259	0.0493
wR2[b]	0.0764	0.0682	0.0695	0.1025	0.2003	0.0674	0.1325

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for reflections with $I > 2\sigma(I)$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and *a* and *b* are constants set by the program.

Synthesis of [{Pd[*κ*^{2}*C*,*N*-C(=NXy)$C_6H_4NH_2$](CNXy)}$_2$(*μ*-I)]TfO (9a). Tl(OTf) (42 mg, 0.12 mmol) was added to a solution of **2a** (140 mg, 0.24 mmol) in CH_2Cl_2 at 0 °C and the resulting suspension warmed to room temperature overnight. After this time the solution was filtered through $MgSO_4$, the solvent removed, and *n*-hexane added to give **9a** as a bright yellow solid. Yield: 100 mg, 70%. Dec pt: 94 °C. IR (Nujol, cm^{-1}): *ν* 3456 (NH), 3376 (NH), 2178 (C≡N), 1640 (NC). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 8.08 (dd, $^3J_{H,H}$ = 7 Hz, $^4J_{H,H}$ = 1.5 Hz, 1 H, H6), 7.63 (dd, $^3J_{H,H}$ = 7 Hz, $^4J_{H,H}$ = 1.5 Hz, 1 H, H3), 7.45 (ddd, $^3J_{H,H}$ = 7 Hz, $^3J_{H,H}$ = 7 Hz, $^4J_{H,H}$ = 1.5 Hz, 1 H, H4 or H5), 7.27 (ddd, $^3J_{H,H}$ = 7 Hz, $^3J_{H,H}$ = 7 Hz, $^4J_{H,H}$ = 1.5 Hz, 1 H, H4 or H5), 7.10 (t, $^3J_{H,H}$ = 8 Hz 1 H, para H Xy), 6.89 (d, $^3J_{H,H}$ = 8 Hz 2 H, meta H's Xy), 6.67 (d, $^3J_{H,H}$ = 8 Hz 2 H, meta H's Xy), 6.23 (t, $^3J_{H,H}$ = 8 Hz 1 H, para H Xy), 6.16 (s, 2 H, NH_2), 2.15 (s, 6 H, 2Me), 2.03 (s, 6 H, 2Me). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): *δ* 150.92, 143.70, 142.50, 133.95, 132.33 (C−H), 130.46, 129.11 (C−H), 128.91, 128.34, 127.75 (C−H), 127.51 (C−H), 127.45 (C−H), 126.87, 126.62 (C−H), 125.22 (C−H), 123.85 (C−H), 120.26 (q, $^1J_{C,F}$ = 318 Hz, CF_3), 19.15 (Me), 18.25 (Me). Anal. Calcd for $C_{49}H_{48}F_3IN_6O_3Pd_2S$: C, 49.14; H, 4.04; N, 7.02; S, 2.68. Found: C, 49.28; H, 4.11; N, 6.71; S, 2.76. Single crystals of **9a** were grown by slow diffusion of *n*-hexane into solutions of **9a** in CH_2Cl_2.

Crystal Structure Determinations. Data Collection. Crystals were mounted in inert oil on a glass fiber and transferred to the diffractometer (Siemens P4 with LT2 low-temperature attachment) as summarized in Table 1. Unit cell parameters were determined from a least-squares fit of ca. 60 accurately centered reflections (9° < 2*θ* < 25°). Data were recorded using *ω* scans. Exceptions: the crystal of **3a** was mounted as above on a Stoe STADI-4 diffractometer; cell constants were refined from ±*ω* angles of 50 reflections in the range 20° < 2*θ* < 23°; data were recorded using *ω*/*θ*-scans. The crystal of **8** was mounted as above on a Bruker SMART 1000 CCD diffractometer; data were recorded using *ω* and *ϕ* scans.

Structure Solution and Refinement. The structures were solved by the heavy-atom method (**2a**, **3a**, **4a**, **6a**, and **10**·1.5CH_2Cl_2) or by direct methods (**8**, **9a**) and refined anisotropically on F^2 (SHELXL-97 program).[65] Hydrogen atoms were included using a riding model or rigid methyl groups, except as indicated below.

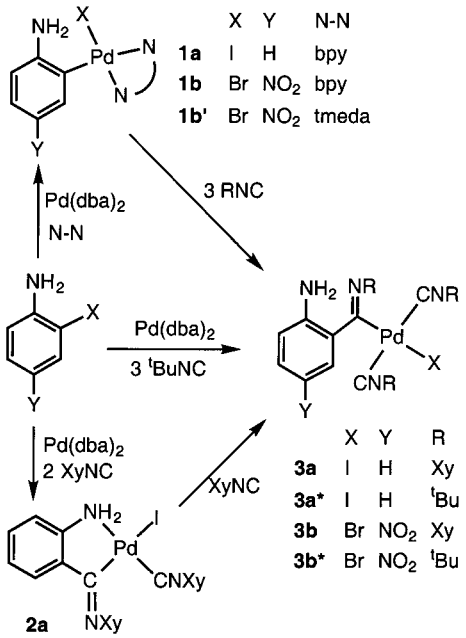
Special Features of Refinement. For compounds **2a**, **3a**, **6a**, and **9a**, the amino group hydrogen atom(s) were located in a difference Fourier synthesis and refined with restrained N−H bond lengths. For compound **4a** the methyl groups C(37) and C(38) are disordered with two sites rotated by 60° from one another (50% occupancy). For compound **6a** the CF_3 group, which is disordered over two sites (65/35% occupancy), was refined with a common carbon position and with isotropic fluorine atoms. The maximum residual electron density of 1.44 e Å^{-3} is associated with the disordered CF_3 group. In compound **8** one butyl group (at C17) and one triflate anion are disordered over two positions. For **10**·1.5CH_2Cl_2 one of the CH_2Cl_2 molecules was refined with a common chlorine and carbon position and with an isotropic chlorine atom disordered over two sites (70/30% occupancy). The maximum residual electron density of 1.38 e Å^{-3} is associated with the disordered CH_2Cl_2. The programs use neutral atom scattering factors, $\Delta f'$ and $\Delta f''$, and absorption coefficients from ref 66.

Results and Discussion

We have previously reported the synthesis of the complex [Pd{$C_6H_4NH_2$-2}I(bpy)] (**1a**; bpy = 2,2′-bipyri-

(65) SHELXL 97; University of Göttingen, Göttingen, Germany.
(66) *International Tables for Crystallography*, Kluwer Academic: Dordrecht, The Netherlands, 1992; Vol. C, Tables 6.1.1.4 (pp 500−502), 4.2.6.8 (pp 219−222), and 4.2.4.2 (pp 193−199).

Scheme 1



dine), by reacting "$Pd(dba)_2$" (dba = dibenzylideneacetone) with 2-iodoaniline in the presence of bpy.[16,17] By a similar procedure, the complexes [Pd{$C_6H_3NH_2$-2-NO_2-5}Br(L_2)] (L_2 = bpy (**1b**), tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (**1b**′)) were obtained. Although **1b** could not be isolated as an analytically pure compound, it could be used as the starting material for the synthesis of several derivatives (Scheme 1).

The reaction of "$Pd(dba)_2$" with XyNC (Xy = 2,6-dimethylphenyl) and then addition of an excess of 2-iodoaniline (1:2:2 molar ratio) yielded the complex [Pd{κ^2C,N-C(=NXy)$C_6H_4NH_2$-2}I(CNXy)] (**2a**) (Scheme 1). When a similar reaction was carried out with ^{t}BuNC (1:2:3 molar ratio, Pd:^{t}BuNC:2-iodoaniline), the complex *trans*-[Pd{C(=N^{t}Bu)$C_6H_4NH_2$-2}I(CN^{t}Bu)$_2$] (**3a***) was obtained (Scheme 1). Therefore, the reaction involves the coordination of three molecules of isonitrile per palladium instead of the two molecules used. Surprisingly, when a 1:3 stoichiometry was used, the yield was lower. Complex **3a*** could also be obtained by reacting **1a** with ^{t}BuNC in a 1:3 molar ratio.

The reaction between ^{t}BuNC and Pd(0) complexes has been shown to give "$Pd(CN^tBu)_2$" (eq 1).[67]

$$\text{“Pd(CN}^t\text{Bu)}_2\text{”} + \text{RX} \rightarrow [\text{Pd(R)X(CN}^t\text{Bu)}_2] \quad (1)$$

$$[\text{Pd(R)X(CN}^t\text{Bu)}_2] \rightarrow {}^2/_3[\text{Pd\{C(=N}^t\text{Bu)R\}X(CNR′)}_2] + {}^1/_3\text{“Pd(R)X”} \quad (2)$$

3a*

Reactions between acyl, aroyl, and alkyl chlorides and "$Pd(CN^tBu)_2$" were reported to give the complexes [Pd(R)X($CN^tBu)_2$] (eq 2, R = MeC(O), PhC(O), $(CH_2)_2CO_2$Et, CH(Ph)CO_2Et, CH_2CO_2Me, X = Cl) but not insertion products.[68] Similar complexes with R = CH_2Ph and X = Br, I were isolated by reacting "$Pd(CN^tBu)_2$" with XR, although with X = Cl, the dinuclear complex [Pd{C(=N^{t}Bu)CH_2Ph}Cl(CN^{t}Bu)]$_2$ was obtained.[59] In our case, the ability of the *o*-NH_2 group to coordinate to the metal atom to form a chelate is responsible for the formation of the mononuclear complex **2a**. However, the reaction with ^{t}BuNC seems to occur by a different mechanism. It seems coordination of a third isonitrile ligand is faster than the formation of the complex homologous to **2a**. However, this does not explain why **3a*** was isolated in lower yield when using stoichiometric amounts of the reagents. We have observed this behavior previously using 2-ROC_6H_4I (R = H, C(O)Me) as the oxidative addition reagent and proposed the following reaction pathway.[62] We assumed that the resulting [Pd(R)I(CN^{t}Bu)$_2$] (or that homologous to **2a**) (eq 1) quickly decomposes to **3a*** and some polymeric complex (eq 2). When a 1:3 molar ratio of Pd to ^{t}BuNC was used, not only does the polymer not react with isonitrile to give **3a*** but other side reactions probably occur as well.

Similar reactions using 2-bromo-4-nitroaniline require higher temperatures than those with 2-iodoaniline in order to achieve the oxidative addition. Unfortunately, this usually led to intractable mixtures. However, the reaction of **1b** or **1b**′ with XyNC or ^{t}BuNC (1:3 molar ratio), respectively, gave the complex **3b** or **3b***, respectively. Similarly, the reaction of **2a** or **1a** with XyNC (1:1 molar ratio) or ^{t}BuNC (1:3 molar ratio), respectively, gave the complex **3a** or **3a***, respectively (Scheme 1). It is noteworthy that in only one case, complex **2a**, does coordination of the NH_2 group occur to give a cyclometalated species. From the reaction of **1b** or **1b**′ with both isonitriles or the reaction of **1a** with ^{t}BuNC in a 1:2 or even a 1:1 molar ratio, only the corresponding complex **3** could be isolated. This also suggests that the resulting complex **2** is unstable and decomposes to give the corresponding complex **3**. This contrasts with previously reported reactions of [PdClMe(L_2)] (L_2 = bidentate nitrogen donor ligand) with isonitriles in a 1:1 molar ratio, affording the monoinserted complexes [PdCl{C(=NR)Me}(L_2)].[21,29] In the case of the NO_2-substituted aryl derivatives, the presence of this electron-withdrawing substituent could explain the decrease of the stability of the corresponding complex **2** due to the reduced coordinating ability of the amino group; this effect has also been observed in the (2-amino-5-nitrophenyl)-palladium and -platinum compounds studied previously.[15,69] Moreover, the reaction of complexes **3** with Tl(TfO) (TfO = CF_3SO_3) led to decomposition products, with the exception of **3a**, which is transformed into the cationic cyclopalladated complex *cis*−[Pd{κ^2C,N-C(=NXy)$C_6H_4NH_2$-2}(CNXy)$_2$]TfO (**4a**) (Scheme 2) involving one inserted and two coordinated XyNC molecules.

Complex **3a*** or **3b*** reacts with ^{t}BuNC and Tl(TfO) to give the cationic species **5a*** or **5b***, respectively, with one inserted and three coordinated isonitriles (Scheme 2). However, similar reactions of **3a** or **3b** with XyNC give TlI and a complex mixture from which we could not identify any product. Complex **3a*** reacts with bpy and Tl(TfO) (1:1.1:1.2) to give the cationic complex **6a***, resulting from the substitution of one isonitrile and the iodo ligands. A similar reaction starting from **3a**, **3b**, or **3b*** resulted in the formation of complex mixtures of

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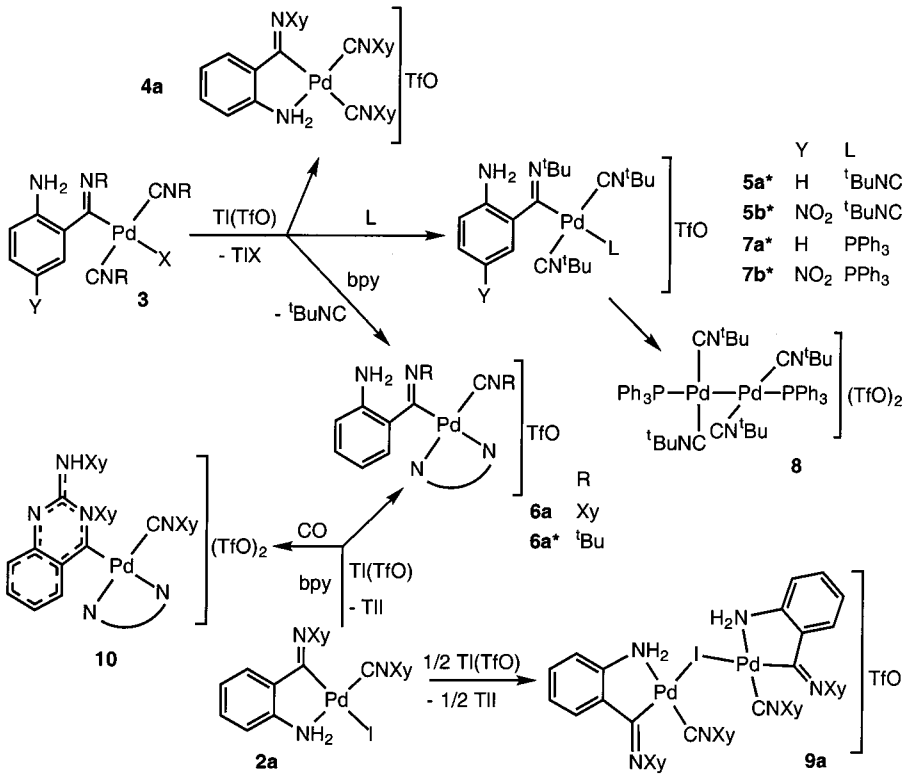
Scheme 2



products. The homologous **6a** was obtained by reacting **2a** with bpy and Tl(TfO) (1:1:1) (Scheme 2). When CO was bubbled for 30 min through the above mixture of **2a**, bpy, and Tl(TfO) (0.68 mmol of each in acetone), a complex mixture of products was obtained. After the removal of TlI, a single crystal was isolated from the solution, which an X-ray diffraction study showed to be the cationic complex $[Pd(R)(CNXy)(bpy)](TfO)_2$ (**10**), where R is 2-(xylylamino)-3-xylylquinazolinium-4-yl (see Scheme 2). Unfortunately, despite repeated attempts, we have not been able to isolate **10** again or the other products of the reaction. It is therefore difficult to propose any explanation for its formation or to elucidate the role played by the carbon monoxide.

The reaction of **3a*** or **3b*** with PPh_3 in the presence of Tl(TfO) gives rise to the formation of *trans*-[Pd{C(=NR)$C_6H_3NH_2$-2-Y-5}($CN^tBu)_2(PPh_3)$]TfO (Y = H (**7a***), NO_2 (**7b***)). These complexes are unstable and decompose slowly, preventing their complete purification. When they were left in solution for 24 h at room temperature, Et_2O was slowly added, and the resulting suspension left overnight in the refrigerator, a mixture was obtained in which single crystals were separated and studied by X-ray diffraction, proving to be the cationic palladium(I) dimer $[Pd_2(CN^tBu)_4(PPh_3)_2](TfO)_2$ (**8**). From the above-mentioned mixture we attempted unsuccessfully to isolate an analytically pure sample of **8**. The mother liquors resulting from this treatment contains a complex mixture of organic and/or organometallic compounds, as revealed by the ^1H NMR spectrum of the corresponding residue obtained by evaporation of the solution to dryness; this may indicate a nonselective radical decomposition process. The NMR resonances in the spectra of **8** appear as impurities in freshly prepared samples of **7a*** or **7b***. The instability of these complexes may be due to the transphobia between a phosphorus donor ligand and the aryl ligand.[17,70,71] Such a destabilizing effect can explain the geometry of some palladium complexes,[71] of some C−X (X = C, N, O, P) coupling processes,[5,17,72] and also of an oxygenation reaction that we have recently reported.[16,17]

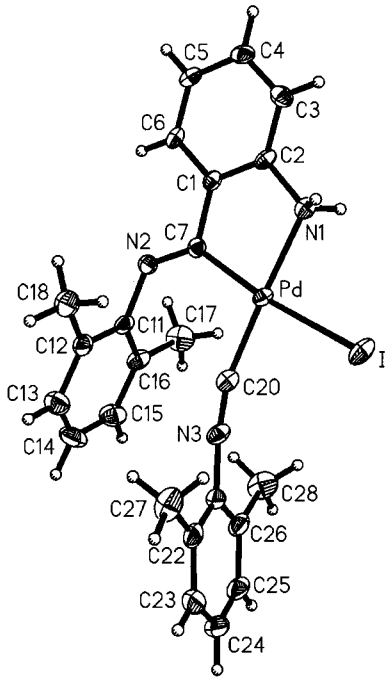


Figure 1. Thermal ellipsoid plot (50% probability level) of **2a**. Selected bond lengths (Å) and angles (deg): Pd−C(20) = 1.941(4), Pd−C(7) = 2.027(4), Pd−N(1) = 2.074(4), Pd−I = 2.6981(5), N(2)−C(7) = 1.268(5); C(20)−Pd−C(7) = 99.66(16), C(20)−Pd−I = 87.23(12), N(1)−Pd−I = 90.27(10), C(7)−Pd−N(1) = 82.88(15), C(7)−N(2)−C(11) = 126.0(3).

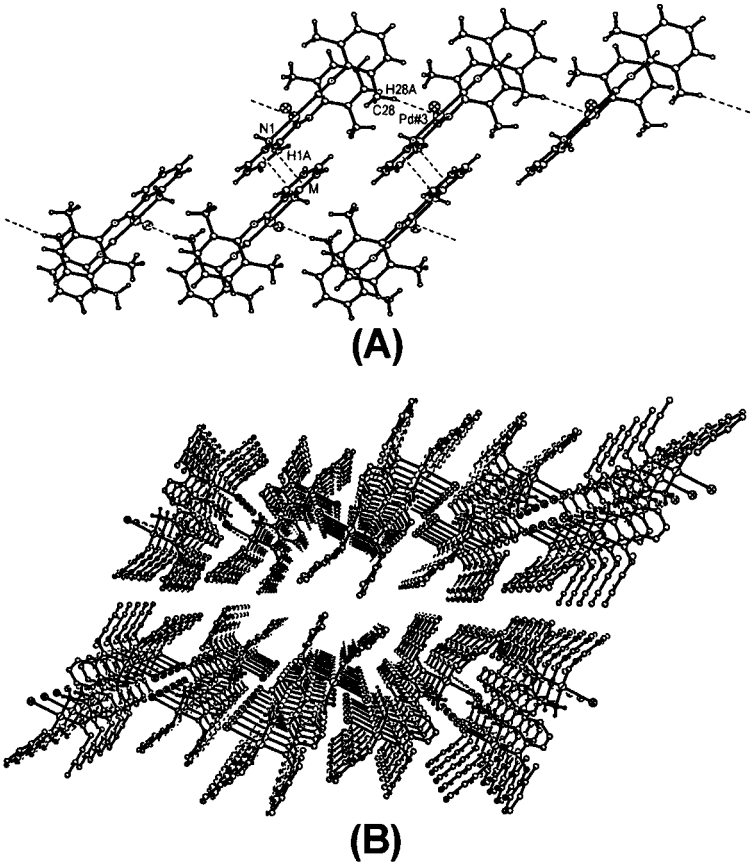


Figure 2. (A) Packing diagram of **2a**, showing C(28)−H(28A)···Pd#3 (#3: $x, y + 1, z$) and N(1)−H(1A)···M (M = centroid of ring C(1)#2 to C(6)#2 (#2: $-x, -y, -z$)) hydrogen bonds. (B) Packing view along the *b* axis of **2a**, showing two molecular layers. Interactions have been omitted for clarity.

The formation of **8** shows a new manifestation of the transphobic effect. Similar palladium(I) complexes $[Pd_2(CNR)_4L_2]^{n+}$ (n = 2, R = Me, L = MeNC;[73−76] n = 2, R = ^{t}Bu, L = ^{t}BuNC;[76] n = 0, R = ^{t}Bu, L = I, Br,[77] Cl;[76−78] n = 0, R = Me, L = I[79]) have been reported. One or two isocyanides in $[Pd_2(CNR)_6]^{2+}$ have preliminarily been reported to be replaced in solution by PPh_3 to give $[Pd_2(CNMe)_{6-n}(PPh_3)_n]^{2+}$ (n = 1, 2).[80]

The reaction of **2a** with Tl(TfO) in a 2:1 molar ratio results in the formation of the binuclear complex [{Pd[κ^2C,N-C(=NXy)$C_6H_4NH_2$](CNXy)}$_2$(μ-I)]TfO (**9a**), which, as confirmed by its X-ray crystal structure, consists of two cyclopalladated moieties connected by a bridging iodine atom. It is surprising that complex **9a** was still obtained even when using a 1:1 molar ratio.

Structure of Complexes. The NMR spectra of the complexes are in agreement with the proposed structures. However, the ^{1}H NMR spectrum of **4a** shows a broad signal corresponding to four Me groups that transforms into two Me singlets at $T < 10$ °C. It is reasonable to assume that the large trans influence of the C-donor ligand favors the dissociation of the XyNC ligand trans to the imidoacyl ligand, leading to an intermolecular exchange of isonitriles. The crystal structure of **4a** confirms the weakening of this bond (see below).

In the crystal structure of complex **2a** (Figure 1), the C(=NXy)$C_6H_4NH_2$-2 ligand is bonded to the palladium atom through both the imine carbon and the amino nitrogen atoms. The cis disposition of the carbon donor ligands is due to the large transphobia between C-donor ligands.[17,70] The structure is planar (mean deviation 0.034 Å), apart from both Xy rings, which are almost perpendicular to the main plane (dihedral angles of 89.5 and 84.2°, respectively), thus avoiding steric hindrance.

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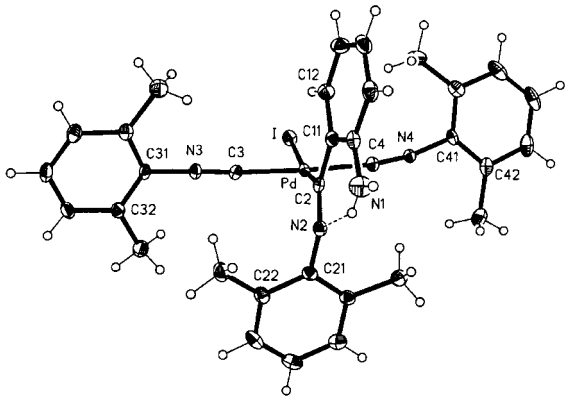

Figure 3. Thermal ellipsoid plot (50% probability level) of **3a**. Selected bond lengths (Å) and angles (deg): I−Pd = 2.7246(9), Pd−C(3) = 1.969(4), Pd−C(4) = 1.985(4), Pd−C(2) = 2.059(4), N(2)−C(2) = 1.264(5), N(3)−C(3) = 1.141-(5), N(4)−C(4) = 1.140(5); C(3)−Pd−C(2) = 88.01(14), C(4)−Pd−C(2) = 90.07(14), C(3)−Pd−I = 93.31(11) C(4)−Pd−I = 87.99(11), C(2)−N(2)−C(21) = 126.5(3), C(3)−N(3)−C(31) = 175.0(4), C(4)−N(4)−C(41) = 169.1(4), N(2)−C(2)−C(11) = 121.2(3), N(2)−C(2)−Pd = 125.5(3), C(11)−C(2)−Pd = 113.2(3), N(3)−C(3)−Pd = 176.9(3), N(4)−C(4)−Pd = 171.9(3).

A C_{sp^3}−H···Pd (C(28)−H(28A)···Pd#3) intermolecular interaction is observed (Figure 2A). The C−H bond approaches the Pd atom from one of the axial positions, which could be interpreted as a hydrogen bond, as occurs in other square-planar complexes of group 10 elements;[81−83] this interaction links molecules to form infinite linear chains parallel to the *b* axis. Pairs of these chains are self-assembled through mutual intermolecular N−H hydrogen bonds with the π system of the arene C(1)#2−C(6)#2 giving a double chain (Figure 2A). The distance of the H atom to the aromatic centroid (M) (H(1A)···M = 2.444 Å) is much shorter than the distances to any of the individual C atoms (distance range 2.61−3.08 Å). Additionally, the angle between the H(1A)···M vector and the normal to the phenyl ring is 11°, showing that the interaction is close to centered.[84] The remaining hydrogen atom of the amino group interacts with an iodine atom of another different molecule (N(1)−H(2A)···I#1). This interaction is readily identified as an N−H···I−Pd hydrogen bond[82,83] and leads to zigzag chains, also parallel to the *b* axis, connecting the double linear chains described above. As a consequence of the three different hydrogen bond types found in the crystal, a superstructure of molecular layers parallel to the *bc* plane is observed (Figure 2B).

Complex **3a** (Figure 3) exhibits a slightly distorted square-planar geometry; the iodine atom lies 0.36 Å out of the plane of Pd, C2, C3, and C4 (mean deviation 0.02 Å). Two hydrogen bonds involve the amine group as donor: the intramolecular N1−H01···N2 (H···N = 2.05-(3) Å, N−H···N = 136(4)°) and the intermolecular N1−H02···I (H···I = 3.04(3) Å, N−H···I = 169(5)°), linking molecules related by the n glide.

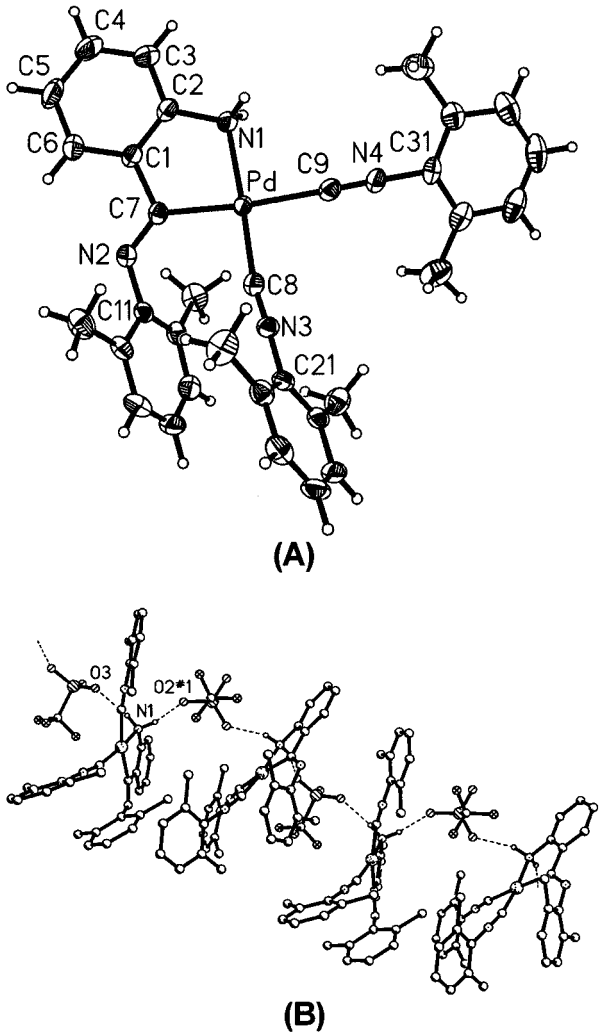

Figure 4. (A) Thermal ellipsoid plot (50% probability level) of the cation of **4a** and (B) N(1)−H(1A)···O(3) and N(1)−H(1B)···O(2)#1 (#1: x, $-y + {}^1/_2$, $z + {}^1/_2$) intermolecular interactions forming zigzag chains. Selected bond lengths (Å) and angles (deg): Pd−C(8) = 1.950(3), Pd−C(7) = 2.034(3), Pd−N(1) = 2.068(2), Pd−C(9) = 2.087(3), N(2)−C(7) = 1.262(3), N(2)−C(11) = 1.399(3), N(3)−C(8) = 1.149-(3), 1.409(3), N(4)−C(9) = 1.144(3); C(8)−Pd−C(7) = 95.28-(11), C(7)−Pd−N(1) = 82.97(10), C(8)−Pd−C(9) = 92.58(11), N(1)−Pd−C(9) = 90.11(10), C(7)−N(2)−C(11) = 125.6(2), C(8)−N(3)−C(21) = 177.1(3), C(9)−N(4)−C(31) = 177.9-(3).

The crystal structure for compound **4a** (Figure 4A) shows the palladium center in a distorted square-planar environment with an angle of 10.8° between the N(1)−Pd−C(7) and C(8)−Pd−C(9) planes. The much greater trans influence exerted by the iminoacyl carbon donor ligand with respect to that of the coordinated NH_2 group is shown by the significantly longer Pd−C(9) bond distance (2.089(3) Å) compared to Pd−C(8) (1.948(3) Å). As mentioned above, the weakening of the Pd−C(9) bond could be the origin of the behavior shown by this complex in solution. Each hydrogen of the amino group acts as a hydrogen bond donor to an oxygen atom of two different triflate anions forming zigzag chains parallel to the *c* axis (N(1)···O(3) = 2.937(3) Å, H(1A)···O(3) 2.0 Å, N(1)−H(1A)···O(3) = 157.4° and N(1)···O(2)#1

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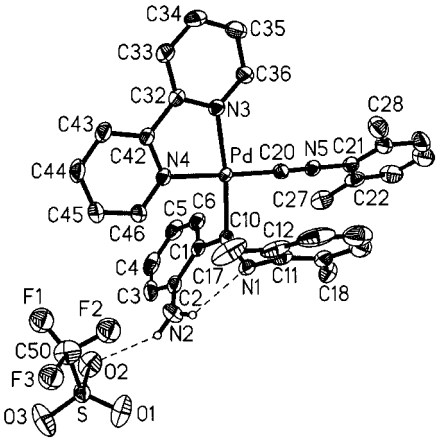

Figure 5. Thermal ellipsoid plot (50% probability level) of **6a** showing N(2)−H(2A)···N(1) and N(2)−H(2B)···O(2) hydrogen bonds. All other hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−C(20) = 1.939(3), Pd−C(10) = 2.015(3), Pd−N(4) = 2.100(3), Pd−N(3) = 2.137(3), N(1)−C(10) = 1.279(5), N(5)−C(20) = 1.146(5); C(20)−Pd−C(10) = 87.32(13), C(10)−Pd−N(4) = 94.44(12), C(20)−Pd−N(3) = 100.19(12), N(4)−Pd−N(3) = 78.05(11), C(10)−N(1)−C(11) = 121.9(3), C(20)−N(5)−C(21) = 178.1(4).

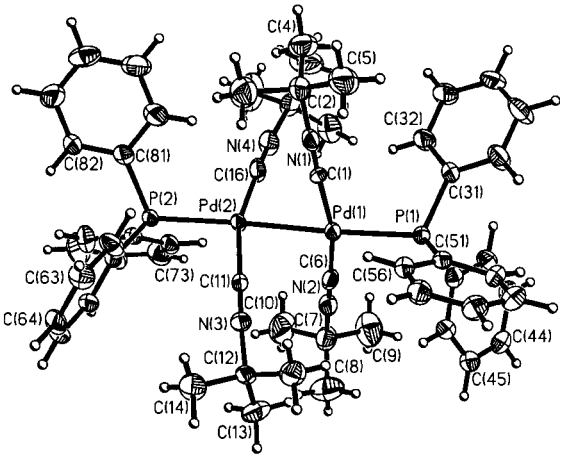

Figure 6. Thermal ellipsoid plot (30% probability level) of the cation of **8**. Pd(1)−C(1) = 1.980(7), Pd(1)−C(6) = 1.979(7), Pd(1)−P(1) = 2.3560(14), Pd(1)−Pd(2) = 2.5596(7), Pd(2)−C(11) = 1.964(5), Pd(2)−C(16) = 1.983(6), Pd(2)−P(2) = 2.3629(14), C(1)−N(1) = 1.126(8), C(6)−N(2) = 1.151(8), C(11)−N(3) = 1.158(7), C(16)−N(4) = 1.140(7); C(1)−Pd(1)−C(6) = 165.7(2), C(1)−Pd(1)−P(1) = 95.55(15), C(6)−Pd(1)−P(1) = 98.09(15), C(11)−Pd(2)−C(16) = 162.9(2), C(11)−Pd(2)−P(2) = 96.80(15), C(16)−Pd(2)−P(2) = 99.69(16).

(#1: x, $-y + {}^1/_2$, $z + {}^1/_2$) = 2.937(3) Å, N(1)−H(1B)···O(2)#1 = 2.07 Å, N(1)−H(1B)···O(2)#1 = 157.4°) (Figure 4B).

Complex **6a** (Figure 5) shows the palladium atom in a square-planar environment. The plane formed by the Pd coordination plane and the bpy ligand (mean deviation 0.039 Å) is almost perpendicular to the aryl amino group (dihedral angle 87.8°). The distance for the Pd−N(3) bond (2.137(3) Å) is longer than for the Pd−N(4) bond (2.100(3) Å). This indicates a greater trans influence of the iminoacyl ligand with respect to the isonitrile ligand. An intramolecular hydrogen bond N−H···N (N(2)···N(1) = 2.828(5) Å, H(2A)···N(1) = 2.24(5) Å, N(2)−H(2A)···N(1) = 126(4)°) forms a half-chair six-membered ring (N(1) 0.55 Å out of the C(10)−C(1)−C(2)−N(2)−H(2A) plane). The remaining hydrogen atom of the amino group is involved in a hydrogen bond to the triflate anion (N(2)···O(2) = 3.100(5) Å, H(2B)···O(2) = 2.35(4) Å, N(2)−H(2B)···O(2) = 148(5)°) (Figure 5).

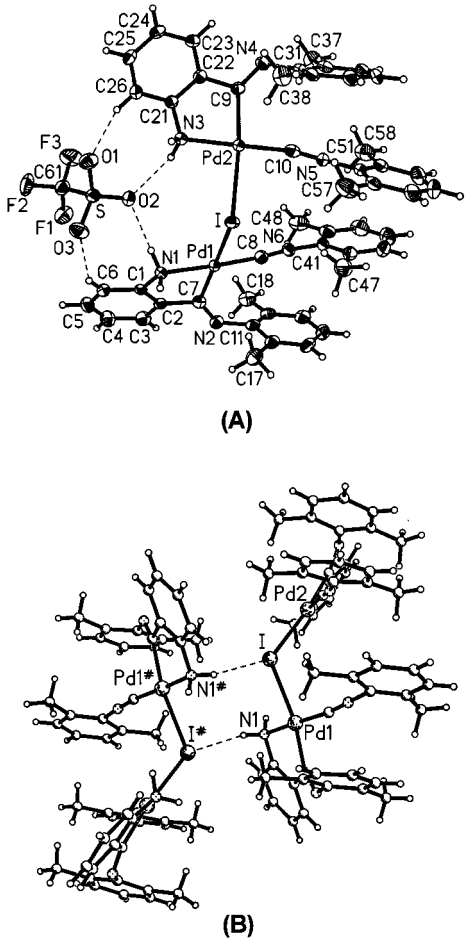

Figure 7. (A) Thermal ellipsoid plot (50% probability level) of **9a** showing N(1)−H(1B)···O(2), N(3)−H(3A)···O(2), C(6)−H(6)···O(1), and C(26)−H(26)···O(3) hydrogen bonds. (B) Dimers of **9a** formed through N(1)−H(1)···I# (#: $-x + 1$, $-y + 1$, $+z + 1$) hydrogen bonds. Selected bond lengths (Å) and angles (deg): I−Pd(2) = 2.7604(3), I−Pd(1) = 2.7680(3), Pd(1)−C(8) = 1.955(3), Pd(1)−C(7) = 2.025(3), Pd(1)−N(1) = 2.095(2), Pd(2)−C(10) = 1.953(3), Pd(2)−C(9) = 2.031(3), Pd(2)−N(3) = 2.088(2), N(2)−C(7) = 1.257(4), N(4)−C(9) = 1.252(4), N(5)−C(10) = 1.154(4), N(6)−C(8) = 1.151(4); Pd(2)−I−Pd(1) = 117.700(10), C(8)−Pd(1)−C(7) = 96.03(12), C(7)−Pd(1)−N(1) = 82.48(11), C(8)−Pd(1)−I = 91.21(9), N(1)−Pd(1)−I = 90.88(7), C(10)−Pd(2)−C(9) = 96.46(12), C(9)−Pd(2)−N(3) = 82.66(11), C(10)−Pd(2)−I = 89.79(9), N(3)−Pd(2)−I = 91.27(7).

The cation of the Pd(I) complex **8** (Figure 6) consists of two Pd atoms, each having a distorted-square-planar geometry. The main distortion is the narrowing of the C−Pd−C angles (162.9(2), 165.7(2)°) in a direction away from the phosphine ligands (P−Pd−C range 95.55(15)−99.69(16)°). In similar complexes with less hindered "axial" ligands, such distortion is less pronounced.[73,79] The Pd−Pd (2.5596(7) Å) and Pd−C bond lengths (1.964(5)−1.983(6) Å) are in the ranges found in structures of related complexes solved with similar accuracy.[73,79,85,86] The angle between the two coordination planes (86.0°) is in the upper limit of the reported data.[73,79,85]

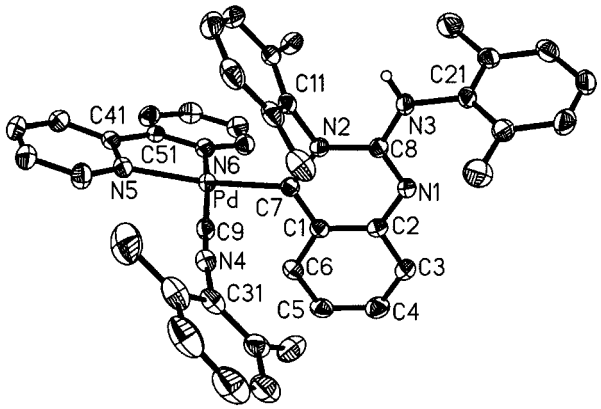

Figure 8. Thermal ellipsoid plot (50% probability level) of the cation of **10**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−C(9) = 1.944(4), Pd−C(7) = 2.009(4), Pd−N(6) = 2.050(4), Pd−N(5) = 2.078(3), N(1)−C(8) = 1.321(5), N(1)−C(2) = 1.361(5), N(2)−C(7) = 1.356(5), N(2)−C(8) = 1.408(5), N(2)−C(11) = 1.461(5), N(3)−C(8) = 1.335(5), N(4)−C(9) = 1.145(5); C(9)−Pd−C(7) = 85.82(16), C(7)−Pd−N(6) = 96.79(15), C(9)−Pd−N(5) = 98.23(15), N(6)−Pd−N(5) = 80.11(14), C(8)−N(1)−C(2) = 118.0(3), C(7)−N(2)−C(8) = 121.6(3), C(7)−N(2)−C(11) = 117.9(3), C(8)−N(2)−C(11) = 120.3(3), C(8)−N(3)−C(21) = 122.2(3), C(9)−N(4)−C(31) = 174.1(4).

The structure of the cation of **9a**·CH_2Cl_2 (Figure 7A) shows an iodine atom bridging two palladium centers, with every palladium atom bonded to both a terminal isonitrile and a chelating C(=NXy)$C_6H_4NH_2$-2 ligand. For both Pd(1) and Pd(2) the C(=NXy)$C_6H_4NH_2$-2 ligand is bonded to the imine carbon trans to iodine and the amino nitrogen atom trans to the isonitrile carbon atom. Such geometry is in accord with the large transphobia between C-donor ligands. The iodine bridge is not symmetric (Pd(1)−I = 2.7680(3) Å and Pd(2)−I = 2.7604(3) Å) and shows an angle Pd(1)−I−Pd(2) of 117.70(1)°. In contrast to compounds **2a** and **4a**, the chelate rings are not planar; angles of 19.5° for the N(1)−C(1)−C(2)−C(7) and N(1)−Pd(1)−C(7) planes and 14.4° for the N(3)−C(21)−C(22)−C(9) and N(3)−Pd(2)−C(9) planes are observed. Both amino groups N(1) and N(3) form a strong hydrogen bond to the O(2) atom of the triflate anion. In addition, there are two weak hydrogen bonds to the remaining oxygen atoms of the triflate anion, C(6)−H(6)···O(1) and C(26)−H(26)···O(3) (Figure 7A) (see the Supporting Information). These supportive hydrogen bonds, forming two ···O−S−O···H−N−C−C−H··· eight-membered rings, could produce the strong distortion found for both chelate rings. In the crystal, dimers are formed through intermolecular N−H···I hydrogen bonds, forming the eight-membered ring I−Pd(1)−N(1)−H(1)···I#−Pd(1)#−N(1)#−H(1)# (#: $-x + 1, -y + 1, +z + 1$) (Figure 7B). A weak C−H···O interaction involving the dichloromethane molecule is also observed (C(62)−H(62B)···O(1)).

The molecular structure of **10**·1.5CH_2Cl_2 (Figure 8) shows a distorted-square-planar palladium environment with a dihedral angle of 11.6° for the planes C(9)−Pd−C(7) and N(8)−Pd−N(6). The bpy ligand is not planar, and the dihedral angle between both rings is 9.2°. The N−C bond distances in the heterocyclic part of the quinazoline ring and the N(3)−C(8) bond length are in a range of 1.321(5)−1.408(5) Å, suggesting a strong electronic delocalization involving these atoms, as indicated in Scheme 2. In fact, the C(11)−N(2)−C(8)−N(3)−C(21) fragment is coplanar with the quinazoline ring (mean deviation 0.038 Å). The amino group N(3)−H(3N) makes a strong hydrogen bond with one O atom of a triflate anion (N(3)···O(4) = 2.907(5) Å, H(3N)···O(4) = 2.03(2) Å, N(3)−H(3N)···O(4) = 163(4)°) and weak C−H···O interactions involving aromatic rings, a solvent molecule and both triflate anions are also observed (see the Supporting Information).

Acknowledgment. We thank the Dirección General de Investigación Científica y Técnica (PB97-1047), INTAS (97-166), and the Fonds der Chemischen Industrie for financial support. A.D.F. and J.L.-S. are grateful to the DGESIC (Spain) and Fundacion Seneca (Comunidad Autonoma de la Region de Murcia, Spain), respectively, for grants.

Supporting Information Available: Listings of all refined and calculated atomic coordinates, all anisotropic thermal parameters, and all bond lengths and angles for compounds **2a, 3a**, **4a**, **6a**, **8**, **9a**·CH_2Cl_2, and **10**·1.5CH_2Cl_2. Crystallographic files for these compounds are also available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0104971

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