Study of the Reactivity of 2-Acetyl-, 2-Cyano-, 2-Formyl-, and 2-Vinylphenyl Palladium(II) Complexes. Mono- and Triinsertion of an Isocyanide into the Pd−C Bond. A 2-Cyanophenyl Palladium Complex as a Ligand

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We have studied the reactivity of the complexes [Pd(C_6H_4X-2)Br(bpy)] (bpy = 2,2′-bipyridine; X = C(O)Me (**1a**), CN (**1b**), CHO (**1c**)), [Pd{C_6H_4CH=CH_2-2}(PPh_3)(bpy)](TfO) (TfO = CF_3SO_3; **2d**), *trans*-[Pd(C_6H_4X-2)Br(PPh_3)$_2$] (X = C(O)Me (**3a**), CN (**3b**), CH=CH_2 (**3d**)), and [Pd(μ-Br)(C_6H_4X-2)(PPh_3)]$_2$(X = C(O)Me (**4a**), CN (**4b**)). Their reactions with XyNC (Xy = 2,6-dimethylphenyl) depend on the nature of X and the other ligands and on the reaction conditions. The products of these reactions are mono- and triinserted complexes. Among the former are [Pd{C(=NXy)C_6H_4X-2}Br(L_2)] (L_2 = bpy, X = C(O)Me (**5a**), CN (**5b**); L = CNXy, X = C(O)Me (**6a**), CN (**6b**), CH=CH_2 (**6d**)) and *trans*-[Pd{C(=NXy)C_6H_4CH=CH_2-2}(CNXy)$_2$(PPh_3)](TfO) (**7d**). The reaction of **1c** with XyNC (1:5 molar ratio) gives **10**, a product resulting after substitution of bpy, coordination of two molecules of XyNC, triinsertion of XyNC, and a cyclization resulting after the attack of the nitrogen of the first inserted molecule at the carbon atom of the formyl group. The complexes [Pd{κ^2C^1,N^3-C(=NXy)C(=NXy)C(=NXy)C_6H_4X-2}Br(CNXy)] (X = C(O)Me (**8a**), CN (**8b**)) were obtained by reacting (i) **3a** or **3b** with XyNC (1:4 molar ratio) or (ii) Pd(dba)$_2$ (dba = dibenzylideneacetone) with BrC_6H_4X-2 and XyNC (1:1:4 molar ratio). When this oxidative addition reaction was carried out with BrC_6H_4CHO-2, the resulting product decomposed to give the Pd(I) complex [Pd_2Br_2(CNXy)$_4$] (**9**). Tl(TfO) was reacted with (i) **8a** and **8b** (1:1 molar ratio) to give the corresponding triflato complexes **11a** and **11b**, (ii) **4a** (1:2 molar ratio) in the presence of moisture to give the cyclopalladated aquo complex [Pd{κ^2C,*O*-C_6H_4[C(O)Me-2}(OH_2)(PPh_3)](TfO) (**12a**), and (iii) **4b** (3:1 molar ratio) to give [Pd(C_6H_4CN-2)(κ^2N,*N*-**4b**)(PPh_3)](TfO) (**13b**), in which **4b** behaves as a ligand through the two cyano groups. The crystal structures of **5b**, **6b**, **7d**, **8a**,**b**, **9**, **10**, **11a**,**b**, **12a**, and **13b** have been determined by X-ray diffraction studies.

Introduction

The chemistry of arylpalladium complexes is a topic of great interest because such compounds participate in many important palladium-catalyzed organic reactions.[1−3] Some of these reactions involve ortho-functionalized aryl complexes that, after insertion of CO, alkenes, or alkynes, give carbo- or heterocycles in which the ortho group is included.[4,5] We have, for example, reported the synthesis of indenols and indenones by reacting (*o*-formylaryl)- or (*o*-acetylaryl)palladium(II) complexes with alkynes.[6−9] A few examples of insertion of isocyanides into ortho-functionalized arylpalladium(II) complexes leading to heterocyclic compounds have also been reported.[10−12] Thus, we have prepared an oxoisoindoline or a family of 2-R-amino-isoindolinium salts by reacting an (*o*-formylaryl)palladium(II) complex[13] or ortho-palladated primary benzylamines,[14] respectively, with isocyanides. The interest of this subject has prompted us to prepare aryl complexes containing ortho-functionalized aryl groups such as $C_6H(OMe)_3$-2,3,4-X-6(X=CHO, C(O)Me, CH_2OEt, C(O)NHBu^t),[13,15−17] $C_6H_3(CHO)_2$-2,5,[18] $C_6H_4NH_2$-2,[19−21] and C_6H_4OH-2,[22] as

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well as cyclopalladated primary and secondary benzylamines.[23−25] Some of these complexes have been used as starting materials in reactions with alkynes,[7,13,17,24,26−28] carbon monoxide,[19,20,22,29] isocyanides,[13,21,22,29] and other unsaturated reagents.[30] Recently, we have reported the synthesis of palladium complexes bearing the aryl groups C_6H_4X-2 (X = CH=CH_2, CHO, C(O)Me, CN).[8] In this work we wish to present the reactivity of these arylpalladium complexes, in particular their reactions with isocyanides. These molecules insert into Pd−C bonds with various results: monoinsertion to give (iminoacyl)palladium derivatives,[13,21,29,31−33] polyinsertion[33,34] including polymeric materials,[35−37] insertion with chemical transformation,[31,38,39] and insertion with chemical transformation and depalladation to give organic products.[10−13,39−41] We also report the crystal structures of most of the prepared complexes, some of which show interesting features.

Experimental Section

The IR (solid state) and NMR spectra, elemental analyses, conductivity measurements in acetone, and melting point determinations were performed as described earlier.[42] "Pd(dba)$_2$" ([$Pd_2(dba)_3$]·dba, dba = dibenzylideneacetone)[1,43] and complexes **1**−**4**[8] were prepared as reported previously. The

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isonitrile XyNC (Xy = 2,6-dimethylphenyl) and the 2-haloarenes were purchased from Fluka. The preparation of complexes was carried out without precautions against light and moisture unless otherwise stated.

Synthesis of [Pd{C(=NXy)C$_6$H$_4$C(O)Me-2}Br(bpy)] (5a). XyNC (86 mg, 0.65 mmol) was added to a solution of [Pd{C$_6$H$_4$-[C(O)Me]-2}Br(bpy)] (**1a**; 300 mg, 0.65 mmol) in CH_2Cl_2 (15 cm^3). The resulting yellow solution was stirred at room temperature for 16 h. The solvent was evaporated and Et_2O (20 cm^3) added, causing the precipitation of orange **5a**. Yield: 325 mg, 84%. Dec pt: 128−130 °C. IR (cm^{-1}): ν(C=O) 1634. ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.11−9.07 (m, 2H), 8.87 (d, 1H, J_{HH} = 5 Hz), 8.0−6.8 (m, 12H), 2.56 (s, MeCO, 3H), 2.13 (bs, Me (Xy), 6H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ 207.6 (C=O), 178.0 (C=N), 155.1 (quaternary C), 152.9 (CH), 152.8 (quaternary C), 150.5 (CH), 148.5 (quaternary C), 141.3 (quaternary C), 138.8 (CH), 138.6 (CH), 138.5 (CH), 135.0 (CH), 128.4 (CH), 128.3 (CH), 127.4 (CH), 127.0 (CH), 126.3 (CH), 123.5 (CH), 122.6 (CH), 121.7 (CH), 121.1 (CH), 31.6 (MeCO), 19.9 (2 Me (Xy)). Anal. Calcd for $C_{27}H_{24}BrN_3OPd$: C, 54.71; H, 4.08; N, 7.09. Found: C, 52.70; H, 4.04; N, 7.07 (see Discussion).

Synthesis of [Pd{C(=NXy)C$_6$H$_4$CN-2}Br(bpy)] (5b). This was similarly prepared from [Pd{C$_6$H$_4$CN-2}Br(bpy)] (**1b**; 100 mg, 0.22 mmol) and XyNC (29 mg, 0.22 mmol): orange **5b**. Yield: 54 mg, 43%. Mp: 112−114 °C dec. IR (cm^{-1}): ν(C≡N) 2214. NMR: not sufficiently soluble. Anal. Calcd for $C_{26}H_{21}BrN_4Pd$: C, 54.24; H, 3.68; N, 9.73. Found: C, 51.67; H, 3.74; N, 9.37 (see Discussion). Single crystals were grown by slow diffusion of Et_2O into a solution of **5b** in CH_2Cl_2.

Synthesis of *trans*-[Pd{C(=NXy)C$_6$H$_4$[C(O)Me]-2}Br(CNXy)$_2$] (6a). Method A. XyNC (342 mg, 2.61 mmol) was added to a solution of **1a** (400 mg, 0.87 mmol) in CH_2Cl_2 (15 cm^3). The resulting yellow solution was stirred at room temperature for 2 h. The solvent was evaporated and Et_2O (20 cm^3) added. The resulting mixture was partially evaporated, a precipitate appearing on cooling; the solid was filtered, washed with cold Et_2O, and air-dried, giving yellow **6a**. Yield: 547 mg, 90%.

Method B. 3a (200 mg, 0.24 mmol) and XyNC (94 mg, 0.72 mmol) were mixed in CH_2Cl_2 (15 cm^3) under nitrogen and the resulting solution evaporated immediately. Et_2O (20 cm^3) was added and the mixture partially evaporated to give a precipitate on cooling; the solid was filtered in air and washed with cold Et_2O, giving **6a**. Yield: 70 mg, 42%.

Method C. 4a (60 mg, 0.05 mmol) and XyNC (41 mg, 0.32 mmol) were mixed in CH_2Cl_2 (15 cm^3) under nitrogen, and the resulting solution evaporated immediately. Et_2O (20 cm^3) was added and then partially evaporated, a precipitate appearing on cooling; the solid was filtered in air and washed with cold Et_2O, giving **6a**. Yield: 54 mg, 74%. Mp: 104 °C. IR (cm^{-1}): ν(C≡N) 2186, ν(C=O) 1690, 1698, ν(C=N) 1628. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (d, 1H, $^3J_{HH}$ = 8 Hz), 7.52 (t, 1H, $^3J_{HH}$ = 8 Hz), 7.42 (t, 1H, $^3J_{HH}$ = 8 Hz), 7.31−7.17 (m, 3H), 7.05−7.0 (m, C$_6$H$_3$, 4H), 6.87 (br, C$_6$H$_3$, 3H), 2.55 (s, MeCO, 3H), 2.19 (s, Me (Xy), 12H), 2.17 (s, Me (Xy), 6H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ 203.8 (C=O), 173.1 (C=N), 149.5 (quaternary C), 143.1 (C≡N), 140.4 (quaternary C), 135.9 (6 quaternary C), 132.6 (CH), 130.0 (CH), 129.4 (CH), 128.9 (CH), 128.0 (2 CH), 127.9 (4 CH), 127.3 (2 quaternary C), 125.5 (CH), 123.5 (CH), 31.2 (MeCO), 18.9 (2 Me (Xy)), 18.5 (4 Me (Xy)). Anal. Calcd for $C_{35}H_{34}BrN_3OPd$: C, 60.14; H, 4.90; N, 6.01. Found: C, 59.87; H, 5.12; N, 6.18.

Synthesis of *trans*-[Pd{C=(NXy)C$_6$H$_4$CN-2}Br(CNXy)$_2$] (6b). Procedures similar to those described for **6a** were followed. Method A: from **1b** (250 mg, 0.56 mmol) and XyNC (220 mg, 1.68 mmol); yellow **6b**. Yield: 359 mg, 94%.

Method B: from **3b** (200 mg, 0.24 mmol) and XyNC (94 mg, 0.72 mmol). Yield: 144 mg, 88%.

Method C: from **4b** (60 mg, 0.054 mmol) and XyNC (41 mg, 0.32 mmol). Yield: 38 mg, 52%. Mp: 136−140 °C dec. IR (cm^{-1}): ν(C≡N) 2224, 2208, 2184, ν(C=N) 1612. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.29 (d, 1H, $^3J_{HH}$ = 8 Hz), 7.75−7.69 (m, 2H), 7.48 (td, 1H, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.26−7.20 (m, 2H), 7.1−7.05 (m, C$_6$H$_3$, 4H), 6.92 (br, C$_6$H$_3$, 3H), 2.24 (s, Me, 12H), 2.22 (s, Me, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 171.3 (C=N), 149.6 (quaternary C), 147.8 (quaternary C), 135.8 (6 quaternary C), 134.0 (CH), 132.2 (CH), 131.5 (CH), 130.2 (CH), 128.8 (CH), 128.1 (2 CH), 128.0 (4 CH), 126.5 (2 quaternary C), 123.7 (CH), 118.7 (quaternary C), 108.8 (quaternary C), 19.0 [2 Me], 18.6 [4 Me]. Anal. Calcd for $C_{34}H_{31}BrN_4Pd$: C, 59.88; H, 4.58; N, 8.22. Found: C, 60.12; H, 4.97; N, 8.58. Single crystals were grown by slow diffusion of *n*-hexane into a solution of **6b** in acetone.

Synthesis of *trans*-[Pd{C(=NXy)C$_6$H$_4$CH=CH$_2$-2}Br(CNXy)$_2$] (6d). This compound was prepared, as described in method B for **6a**, from **3d** (200 mg, 0.24 mmol) and XyNC (94 mg, 0.72 mmol). Yield: 123 mg, 75%. This complex darkens on exposure to daylight. Mp: 90 °C dec. IR (cm^{-1}): ν(C≡N) 2180, ν(C=N) 1626. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92−7.89 (m, 1H), 7.76 (dd, C*H*=CH$_2$, 1H, $^3J_{HH}$ = 17 Hz, $^3J_{HH}$ = 11 Hz), 7.56−7.53 (m, 1H), 7.38−7.30 (m, 2H), 7.24−7.19 (m, 2H), 7.07−7.04 (m, C$_6$H$_3$, 4H), 6.93−6.86 (m, C$_6$H$_3$, 3H), 5.61 (d, CH=C*H*$_2$ trans to H, 1H, $^3J_{HH}$ = 17 Hz), 5.34 (d, CH=C*H*$_2$ cis to H, 1H, $^3J_{HH}$ = 11 Hz), 2.24 (s, Me, 6H), 2.22 (s, Me, 12H). ^{13}C{^{1}H} NMR: the compound decomposes during the experiment. Anal. Calcd for $C_{35}H_{34}BrN_3Pd$: C, 61.55; H, 5.02; N, 6.15. Found: C, 60.81; H, 4.96; N, 6.01.

Synthesis of *trans*-[Pd{C(=NXy)C$_6$H$_4$CH=CH$_2$-2}(CNXy)$_2$(PPh$_3$)](TfO) (7d). Complex **2d** (200 mg, 0.27 mmol) and XyNC (104 mg, 0.81 mmol) were reacted under nitrogen for 1 h. The solvent was evaporated in vacuo and Et_2O (20 cm^3) added. The resulting mixture was partially evaporated, a precipitate appearing on cooling; the solid was filtered, washed with cold Et_2O, and air-dried, giving yellow **7d**. Yield: 254 mg, 94%. Mp: 110 °C dec. IR (cm^{-1}): ν(C≡N) 2196, 2176, ν(C=N) 1618. Λ_M (acetone): 136 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.7−7.2 (m, 20H), 7.1−7.0 (m, C$_6$H$_3$, 9H), 5.66 (d, CH=C*H*$_2$ trans to H, 1H, $^3J_{HH}$ = 17 Hz), 5.35 (d, CH=C*H*$_2$ cis to H, 1H, $^3J_{HH}$ = 11 Hz), 2.18 (s, Me, 6H), 1.74 (s, Me, 12H). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 11.8 (s). Anal. Calcd for $C_{54}H_{49}F_3N_3O_3PPdS$: C, 63.94; H, 4.87; N, 4.14; S, 3.16. Found: C, 63.72; H, 5.10; N, 4.52; S, 2.96. Single crystals were grown by vapor diffusion of Et_2O into a solution of **7d** in CH_2Cl_2.

Synthesis of [Pd{κ^2*C*^{1},*N*^{3}-C(=NXy)C(=NXy)C(=NXy)-C$_6$H$_4$C(O)Me-2}Br(CNXy)] (8a). Method A. *o*-Bromoacetophenone (0.070 cm^3, 0.52 mmol) was added under nitrogen to a suspension of "Pd(dba)$_2$" (200 mg, 0.35 mmol) and XyNC (184 mg, 1.4 mmol) in toluene (15 cm^3). The suspension was refluxed for 5 h and then stirred at room temperature for 16 h. After this time the workup is carried out in air. The solvents were evaporated, the residue was extracted with CH_2Cl_2, and the extract was filtered over anhydrous $MgSO_4$. The resulting red solution was evaporated and the residue triturated with Et_2O (15 cm^3). The precipitate was filtered, washed with Et_2O (2 × 5 cm^3), and air-dried, giving yellow **8a**. Yield: 183 mg, 63%.

Method B. Complex **3a** (60 mg 0.07 mmol) and XyNC (38 mg, 0.29 mmol) were mixed in CH_2Cl_2 (15 cm^3) under nitrogen and stirred at room temperature for 20 h. The initially yellow solution turned red after a few hours. The solvent was evaporated and the residue triturated with Et_2O (20 cm^3), giving a solid, which was isolated by filtration. This solid was purified by means of silica gel (70−200 μm) preparative TLC chromatography using acetone/*n*-hexane (1:2) as eluant. The fraction at R_f = 0.4 was collected and extracted with acetone to give a solution which was evaporated to dryness. The

(43) Takahashi, Y.; Ito, S.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065.

residue was redissolved in CH_2Cl_2 (15 cm^3), and anhydrous $MgSO_4$ was added. The resulting suspension was stirred for 1 h and filtered. The solution was evaporated, Et_2O was added, and the precipitate was filtered, washed with Et_2O (2 × 5 cm^3), and air-dried to give **8a**. Yield: 23 mg, 41%.

Method C. 8a was similarly prepared from **4a** (60 mg, 0.05 mmol) and XyNC (52 mg, 0.40 mmol). Yield: 34 mg, 42%. Dec pt: 243 °C. IR (cm^{-1}): ν(C≡N) 2190, ν(C═O) 1676, ν(C═N) 1644. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97−7,94 (m, 1H), 7.52−7.44 (m, 2H), 7.29−7.27 (m, 1H), 7.1−6.75 (m, 10H), 6.35−6.28 (m, 2H), 2.73 (s, Me, 3H), 2.66 (s, Me, 3H), 2.64 (s, Me, 3H), 2.21 (s, Me, 3H), 2.16 (s, Me (Xy), 6H), 2.08 (s, Me, 3H), 1.90 (s, Me, 3H), 1.09 (s, Me, 3H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ 197.1 (C═O), 176.3 (C═N), 172.3 (C═N), 169.2 (C═N), 151.0 (quaternary C), 147.6 (quaternary C), 143.6 (quaternary C), 135.9 (quaternary C), 134.6 (quaternary C), 132.6 (CH), 132.1 (quaternary C), 131.1 (quaternary C), 130.5 (CH), 129.2 (quaternary C), 129.1 (CH), 128.9 (CH), 128.2 (CH), 127.6 (CH), 127.4 (CH), 127.35 (CH), 127.3 (CH), 126.7 (CH), 126.6 (CH), 126.1 (quaternary C), 123.7 (CH), 123.3 (CH), 121.8 (quaternary C), 27.1 (MeCO), 20.5 (Me (Xy)), 19.9 (Me (Xy)), 18.6 (3 Me (Xy)), 18.4 (2 Me (Xy)), 17.4 (Me (Xy)). Anal. Calcd for $C_{44}H_{43}BrN_4OPd$: C, 63.66; H, 5.22; N, 6.75. Found: C, 63.36; H, 5.32; N, 6.91. Single crystals were grown by slow diffusion of *n*-hexane into a solution of **8a** in CH_2Cl_2.

Synthesis of [Pd{κ^2-*C*^{1},*N*^{3}-C(═NXy)C(═NXy)C(═NXy)-C$_6$H$_4$CN-2}Br(CNXy)] (8b). Method A. Red **8b** was prepared as described for **8a** from "Pd(dba)$_2$" (300 mg, 0.52 mmol), XyNC (274 mg. 2.09 mmol), and *o*-bromobenzonitrile (142 mg, 0.78 mmol). Yield: 271 mg, 64%.

Method B. Complex **3b** (70 mg 0.09 mmol) and XyNC (34 mg, 0.27 mmol) were mixed in CH_2Cl_2 (15 cm^3) under nitrogen and stirred at room temperature for 20 h. The initially yellow solution turns red after a few hours. The solvent was evaporated and the residue triturated with Et_2O (20 cm^3), giving a red solid which was filtered, washed with Et_2O, and air-dried. Yield: 22 mg, 30%.

Method C. 8b was prepared by following the same procedure from **4b** (60 mg, 0.05 mmol) and XyNC (52 mg, 0.4 mmol). Yield: 32 mg, 39%. Dec pt: 148−150 °C. IR (cm^{-1}): ν(C≡N) 2224, 2194, ν(C═N) 1642. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78−7.72 (m, 1H), 7.50−7.44 (m, 2H), 7.25−7.17 (m, 1H), 7.12−6.78 (m, 10H), 6.43−6.41 (m, 1H), 6.33 (t, 1H, $^3J_{HH}$ = 7 Hz), 2.63 (s, Me, 3H), 2.29 (s, Me, 3H), 2.28 (s, Me, 3H), 2.25 (s, Me, 3H), 2.15 (s, Me (Xy), 6H), 2.14 (s, Me, 3H), 1.36 (s, Me, 3H). Anal. Calcd for $C_{43}H_{40}BrN_5Pd$: C, 63.51; H, 4.96; N, 8.61. Found: C, 63.57; H, 4.97; N, 8.53.

Synthesis of [Pd$_2$Br$_2$(CNXy)$_4$] (9). This compound was prepared, by following the procedure A described for **8a**, from "Pd(dba)$_2$" (300 mg, 0.52 mmol), XyNC (274 mg, 2.09 mmol), and *o*-bromobenzaldehyde (0.09 cm^3, 0.78 mmol). In this case, the isolated yellow solid is identified as **9**, which had previously been described.[44] Yield: 166 mg, 71%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25−7.09 (m, 12 H), 2.52 (s, Me, 24H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ 142.9 (C≡N), 135.6 (*C*Me), 129.8 (CH), 128.0 (CH), 126.4 (*C*NC), 19.1 (Me). Single crystals were grown by slow diffusion of *n*-hexane into a solution of **9** in CH_2Cl_2.

Synthesis of 10. XyNC (440 mg, 3.35 mmol) was added under nitrogen to a solution of **1c** (300 mg, 0.67 mmol) in acetone (20 cm^3). The resulting suspension was stirred for 16 h. The solid thus formed was filtered in air, washed with acetone (10 × 10 cm^3), and dried in air to give deep orange **10**. Yield: 214 mg, 34%. Dec pt: 150−152 °C. IR (cm^{-1}): ν(C≡N) 2178, 2 ν(C═O) 1704, ν(C═N) 1672. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.42 (d, 1H, $^3J_{HH}$ = 8 Hz), 8.00 (d, 1H, $^3J_{HH}$ = 7 Hz), 7.61 (td, 1H, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.53 (t, 1H, $^3J_{HH}$ = 7 Hz), 7.19−7.14 (m, 2H), 7.01−6.93 (m, 7H), 6.77−6.71 (m, 3H), 6.65−6.31 (m, 2H), 6.56−6.51 (m, 1H), 2.65 (s, Me, 6H), 2.19 (s, Me, 12H), 1.96 (s, Me, 6H), 1.95 (s, Me, 6H). Anal. Calcd for $C_{52}H_{50}BrN_5OPd$: C, 65.93; H, 5.32; N, 7.39. Found: C, 64.49; H, 5.18; N, 7.22 (see Discussion). Single crystals were grown by slow diffusion of *n*-pentane into a solution of **10** in CH_2Cl_2.

Synthesis of [Pd{κ^2-*C*^{1},*N*^{3}-C(═NXy)C(═NXy)C(═NXy)-C$_6$H$_4$C(O)Me-2}(OTf)(CNXy)] (11a). Tl(TfO) (69 mg, 0.19 mmol) was added to a solution of **8a** (162 mg, 0.19 mmol) in CH_2Cl_2 (15 cm^3). The resulting suspension was stirred for 19 h and filtered over Celite and the orange-red filtrate concentrated (ca. 2 cm^3). Et_2O (15 cm^3) was added, causing the precipitation of a yellow solid, which was filtered, washed with Et_2O (2 × 5 cm^3), and air-dried to give yellow **11a**. Yield: 125 mg, 72%. Dec pt: 165−170 °C. IR (cm^{-1}): ν(C≡N) 2202, ν(C═O), ν(C═N) 1672, 1644. Λ_M (acetone): 124 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (dd, 1 H, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.56−7.45 (m, 2 H), 7.22−6.80 (m, 10 H), 6.49 (t, 1 H, $^3J_{HH}$ = 7 Hz), 6.24 (br d, 2 H, $^3J_{HH}$ = 7 Hz), 2.80 (s, Me, 3H), 2.67 (s, Me, 3H), 2.66 (s, Me, 3H), 2.24 (s, Me, 3H), 2.16 (s, Me (Xy), 6H), 2.03 (s, Me, 3H), 1.90 (s, Me, 3H), 0.98 (s, Me, 3H). Anal. Calcd for $C_{45}H_{43}F_3N_4O_4PdS$: C, 60.10; H, 4.82; N, 6.13; S, 3.57. Found: C, 60.08; H, 4.90; N, 6.19; S, 3.13. Single crystals were grown by slow diffusion of *n*-hexane into a solution of **11a** in chloroform.

Synthesis of [Pd{κ^2-*C*^{1},*N*^{3}-C(═NXy)C(═NXy)C(═NXy)-C$_6$H$_4$CN-2}(OTf)(CNXy)] (11b). Red **11b** was similarly prepared from **8b** (100 mg, 0.12 mmol) and Tl(TfO) (44 mg, 0.12 mmol). Yield: 82 mg, 77%. Dec pt: 255−7 °C. IR (cm^{-1}): ν(C≡N) 2226, 2210, ν(C═N) 1660, 1634. Λ_M (acetone): 112 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80−7.78 (m, 1H), 7.56−7.48 (m, 2H), 7.19−6.88 (m, 11H), 6.49 (t, 1H, $^3J_{HH}$ = 8 Hz), 6.36 (br d, 2H, $^3J_{HH}$ = 8 Hz), 2.63 (s, Me, 3H), 2.40 (s, Me, 3H), 2.27 (s, Me, 3H), 2.25 (s, Me, 3H), 2.20 (s, Me, 3H), 2.17 (s, Me, 6H), 1.23 (s, Me, 3H). Anal. Calcd for $C_{44}H_{40}F_3N_5O_3PdS$: C, 59.90; H, 4.57; N, 7.94; S, 3.63. Found: C, 60.11; H, 4.74; N, 8.06; S, 3.20. Single crystals were grown by slow diffusion of *n*-hexane into a solution of **11b** in CH_2Cl_2.

Synthesis of [Pd{κ^2-*C*,*O*-C$_6$H$_4$[C(O)Me]}(OH$_2$)(PPh$_3$)](TfO) (12a). Tl(TfO) (311 mg, 0.44 mmol) was added to a solution of **4a** (250 mg, 0.22 mmol) in CH_2Cl_2 (15 cm^3). The resulting suspension was stirred for 1 h and then filtered over Celite. The brown filtrate was concentrated to dryness. Et_2O (15 cm^3) was then added, leading to a precipitate that was filtered, washed with Et_2O (2 × 5 cm^3), and air-dried, giving brown **12a**. Yield: 220 mg, 77%. Dec pt: 128−130 °C. IR (cm^{-1}): ν(OH) 3386, ν(C═O) 1582. Λ_M (acetone): 123 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72−7.66 (m, 6H), 7.53−7.38 (m, 10H), 7.04 (t, 1H, $^3J_{HH}$ = 8 Hz), 6.75 (t, 1H, $^3J_{HH}$ = 7 Hz), 6.33 (t, 1H, $^3J_{HH}$ = 8 Hz), 2.73 (s, Me, 3H), 1.82 (s, H_2O, 2H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ 216.6 (C═O), 154.62 (CPd), 147.9 (*C*C(O)Me), 138.0 (d, C6 C_6H_4, $^3J_{PC}$ = 10 Hz), 135.0 (d, ortho C's PPh_3, $^2J_{PC}$ = 12 Hz), 134.7 (CH, C_6H_4), 132.0 (d, ipso C's PPh_3, $^1J_{PC}$ = 26 Hz), 131.8 (para C's PPh_3), 128.8 (d, meta C's PPh_3, $^3J_{PC}$ = 11 Hz), 127.5 (CH, C_6H_4), 125.3 (CH, C_6H_4), 120.0 (q, CF_3, $^1J_{FC}$ = 318 Hz), 24.8 (Me). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 46.1. Anal. Calcd for $C_{27}H_{24}F_3O_5PPdS$: C, 49.51; H, 3.69; S, 4.90. Found: C, 49.70; H, 3.64; S, 5.27. Single crystals were grown by slow diffusion of *n*-hexane into a solution of **12a** in acetone.

Synthesis of [Pd(C$_6$H$_4$CN-2)(κ^2-*N*,*N*-4b)(PPh$_3$)](TfO) (13b). Tl(TfO) (64 mg, 0.18 mmol) was added to a solution of **4b** (100 mg, 0.09 mmol) in CH_2Cl_2 (15 cm^3). The mixture was stirred for 40 min and then filtered over Celite. The resulting yellow solution was evaporated and Et_2O (15 cm^3) added, causing the precipitation of a yellow solid, which was filtered and washed with Et_2O (2 × 5 cm^3) to give yellow **13b**. It was purified by recrystallization from CH_2Cl_2/*n*-hexane. Yield: 79 mg, 76%. Dec pt: 148−150 °C. IR (cm^{-1}): ν(C≡N) 2248, 2214 (sh). Λ_M (acetone): 117 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65−6.47 (m, 57H), 6.08 (d, 1H, $^3J_{HH}$ = 8 Hz), 5.68

(44) Duravila, V.; Mingos, D. M. P.; Vilar, R.; White, A. J. P.; Williams, D. J. *J. Organomet. Chem.* **2000**, *600*, 198.

Table 1. Details of Data Collection and Structure Refinement for the Complexes 5b, 6b, 7d, and 8a·½CH_2Cl_2

	5b	6b	7d	8a·½CH_2Cl_2
formula	$C_{26}H_{21}BrN_4Pd$	$C_{34}H_{31}BrN_4Pd$	$C_{54}H_{49}F_3N_3O_3PPdS$	$C_{44.5}H_{44}BrClN_4OPd$
cryst habit	yellow needle	pale yellow lath	yellow prism	orange tablet
cryst size (mm)	0.28 × 0.08 × 0.08	0.5 × 0.08 × 0.025	0.36 × 0.2 × 0.17	0.29 × 0.28 × 0.20
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1$	$P\bar{1}$
a (Å)	9.7317(6)	16.1064(18)	11.9833(8)	8.1189(6)
b (Å)	12.8158(8)	8.1967(10)	14.9230(12)	11.4137(8)
c (Å)	18.5065(12)	24.146(3)	13.5773(10)	21.9267(14)
α (deg)	90	90	90	95.774(3)
β (deg)	103.138(3)	108.072(3)	98.407(3)	92.752(3)
γ (deg)	90	90	90	98.372(3)
V (Å^3)	2247.7	3030.4	2401.9	1996.0
Z	4	4	2	2
ρ_{calcd} (Mg m^{-3})	1.701	1.495	1.403	1.452
M_r	575.78	681.94	1014.39	872.60
F(000)	1144	1376	1044	890
T (°C)	−130	−130	−130	−130
$2\theta_{max}$ (deg)	56.5	52.7	60	60
μ(Mo Kα) (mm^{-1})	2.6	2.0	0.52	2.07
abs cor	SADABS	SADABS	none	face indexing
transmissn	0.69/0.89	0.52/0.98		0.65/0.77
no. of rflns				
measd	38 774	35 032	51 700	39 038
unique	5569	6202	14 044	11 633
R_{int}	0.057	0.092	0.057	0.045
R^a ($F > 4\sigma(F)$)	0.025	0.033	0.029	0.029
$R_w{}^b$ (F^2, all rflns)	0.064	0.073	0.062	0.073
no. of params	291	367	634	496
no. of restraints	0	90	554	468
S^c	1.03	0.93	1.00	1.05
max $\Delta\rho$ (e Å^{-3})	0.67	0.63	0.60	0.69

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

(d, 2H, $^3J_{HH}$ = 8 Hz). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 31.8 and 31.6 (AB system, $^4J_{PP}$ = 5 Hz); 31.8 and 31.0 (AB system, $^4J_{PP}$ = 5 Hz), 28.3 (s), 28.8 (s). Anal. Calcd for $C_{76}H_{57}Br_2F_3N_3O_3P_3Pd_3S$: C, 53.03; H, 3.34; N, 2.44; S, 1.86. Found: C, 52.76; H, 3.34; N, 2.48; S, 1.57. Single crystals of the trans isomer were grown by slow diffusion of *n*-hexane into a solution of **13b** in CH_2Cl_2.

X-ray Structure Determinations. Details of data collection and refinement are given in Tables 1−3. All compounds were measured on a Bruker SMART 1000 CCD/LT3 instrument. Structures were refined anisotropically on F^2 using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen). Hydrogen atoms were included using a riding model or rigid methyl groups. Disordered groups were refined using appropriate systems of similarity restraints.

Special Features of Refinement. Compound 7d. The triflate anion is disordered over two positions with occupancies of ca. 4:1; the Flack parameter was refined to 0.017(10).

Compound 8a. The solvent is disordered over two pairs of positions related by an inversion center.

Compound 8b. The solvent is disordered over an inversion center. Compounds **8a**,**b** are isostructural, although the conventional cell settings lead to different angles.

Compound 9. The methyl group at C37 converged slowly and may be rotationally disordered.

Compound 11a. The solvent is disordered over an inversion center.

Compound 11b. The triflate is disordered over two positions with occupancies of ca. 2:1; the site O(1) (coordinated to Pd) was assumed to be common to both components, but the Pd−O bond length should be interpreted with caution. The Flack parameter was refined to −0.027(11).

Compound 12a. The water H atoms were refined freely, but with O−H distance restraints.

Compound 13b. The anion and the ring C31−N3 are both disordered over two positions with occupancies of ca. 9:1.

Results and Discussion

Reactivity of Complexes toward XyNC. We have studied the reactions of XyNC (Xy = $C_6H_3Me_2$-2,6) with the complexes [Pd(C_6H_4X-2)Br(bpy)] (X = C(O)Me (**1a**), CN (**1b**), CHO (**1c**)), [Pd($C_6H_4CH{=}CH_2$-2)(PPh_3)(bpy)]OTf (OTf = $CF_3SO_3^-$; **2d**) [Pd(C_6H_4X-2)Br(PPh_3)$_2$] (X = C(O)Me (**3a**), CN (**3b**), CH=CH_2 (**3d**)) and [Pd(C_6H_4X-2)(μ-Br)(PPh_3)]$_2$ (X = C(O)Me (**4a**), CN (**4b**)) using different molar ratios and reaction conditions. The obtained products are the result of mono- or tri-insertion processes.

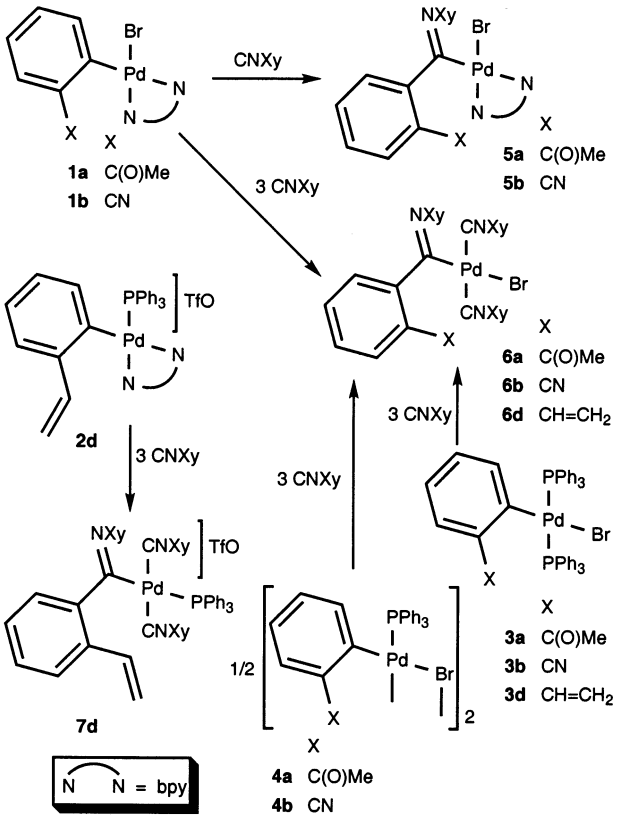
Synthesis of Monoinserted Complexes. When complexes **1a**,**b** were reacted with XyNC in a 1:1 molar ratio, the monoinserted complexes [Pd{C(=NXy)C_6H_4X-2}Br(bpy)] (X = C(O)Me (**5a**), CN (**5b**)) were isolated (Scheme 1). The carbon analyses of both compounds deviate somewhat from the expected values (**5a**, calcd C 54.71, found C 52.70; **5b**, calcd C 54.24, found C 51.67), despite many recrystallizations. Because H and N analyses were acceptable (Anal. Calcd for **5a**: H, 4.08; N, 7.09. Found: H, 4.04; N, 7.07. Anal. Calcd for **5b**: H, 3.68; N, 9.73. Found: H, 3.74; N, 9.37), the ^1H and ^{13}C NMR spectra of **5a** did not show the presence of impurities (complex **5b** was not sufficiently soluble for NMR measurements), and the X-ray crystal structure of **5b** was solved (single crystals of **5b** were also analyzed), we believe that the disagreement between calculated and found carbon analyses are attributable to a combustion problem of the samples.

Table 2. Details of Data Collection and Structure Refinement for the Complexes 8b·$^1/_2CH_2Cl_2$, 9, 10·CH_2Cl_2, and 11a·$^1/_2CHCl_3$

	8b·$^1/_2CH_2Cl_2$	**9**	**10**·CH_2Cl_2	**11a**·$^1/_2CHCl_3$
formula	$C_{43.5}H_{41}BrClN_5Pd$	$C_{36}H_{36}Br_2N_4Pd_2$	$C_{53}H_{52}BrCl_2N_5OPd$	$C_{45.5}H_{43.5}Cl_{1.5}F_3N_4O_4PdS$
cryst habit	red prism	yellow tablet	yellow column	yellow hexagonal tablet
cryst size (mm)	0.28 × 0.18 × 0.12	0.30 × 0.16 × 0.05	0.24 × 0.22 × 0.18	0.35 × 0.25 × 0.11
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	triclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	8.2200(6)	9.7060(10)	12.3762(8)	8.0966(6)
b (Å)	11.7082(8)	11.5432(12)	20.5074(14)	11.7951(8)
c (Å)	21.7552(14)	15.7993(16)	19.8313(12)	23.3677(14)
α (deg)	83.784(3)	94.772(3)	90	88.457(3)
β (deg)	87.266(3)	92.936(3)	106.570(3)	88.833(3)
γ (deg)	70.898(3)	92.903(3)	90	81.515(3)
V (Å^3)	1966.7	1759.0	4824.5	2206.1
Z	2	2	4	2
ρ_{calcd} (Mg m^{-3})	1.445	1.694	1.421	1.444
M_r	841.22	897.31	1032.21	958.98
F(000)	870	884	2112	982
T (°C)	−130	−130	−130	−100
$2\theta_{max}$ (deg)	61	60	56.5	60
μ(Mo Kα) (mm^{-1})	1.6	3.3	1.4	0.62
abs cor	face indexing	SADABS	SADABS	face indexing
transmissn	0.70−0.85	0.71−0.93	0.85−0.96	0.84−0.93
no. of rflns				
measd	43 441	34 438	76 734	43 217
unique	11 961	10 238	11 965	12 860
R_{int}	0.064	0.029	0.051	0.034
R^a ($F > 4\sigma(F)$)	0.033	0.024	0.039	0.038
$R_w{}^b$ (F^2, all rflns)	0.080	0.061	0.120	0.111
no. of params	477	405	578	554
no. of restraints	1	0	0	0
S^c	1.02	0.98	1.05	1.04
max $\Delta\rho$ (e Å^{-3})	0.96	0.54	1.0	1.3

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

Scheme 1



When **1a**,**b** were reacted with XyNC in a 1:X ($X \geq 3$) molar ratio, the compounds *trans*-[Pd{C(=NXy)-C_6H_4X-2}Br$(CNXy)_2$] (X = C(O)Me (**6a**), CN (**6b**)) were obtained (Scheme 1). They resulted from insertion of one isocyanide into the carbon−palladium bond and the displacement of bpy by two isocyanide ligands. This kind of complex is very poorly represented in the literature, the only examples being those recently prepared by us.[14,21,22] The analogous reaction starting from **1c** gave an intractable mixture. The cationic complex **2d** reacts similarly to give *trans*-[Pd{C(=NXy)C_6H_4CH=CH_2-2}-$(CNXy)_2(PPh_3)$](TfO) (**7d**). Complexes **6a**,**b** were also obtained by reacting **3a**,**b** or **4a**,**b** with XyNC in a 1:3 molar ratio, but only when reactions were carried out in CH_2Cl_2 under nitrogen, and were stopped almost immediately after mixing the reactants. This method also allowed the preparation of complex **6d** (X = CH=CH_2) by starting from **3d**. **6d** darkens on exposure to sunlight, although the NMR spectra remain the same. Under aerobic conditions or if the reaction time is extended, complexes **6a**,**b**,**d** were not obtained (see below). The presence in solution of the displaced PPh_3 could be responsible for this behavior; indeed, complex mixtures were formed when **6a**,**b** were reacted with PPh_3.

Synthesis of Triinserted Complexes. Under the same reaction conditions leading to **6a**,**b** from **3a**,**b** or **4a**,**b** and XyNC, but with a longer reaction time (20 h) and in a 1:4 molar ratio, the triinserted complexes [Pd-{κ^2C^1,N^3-C(=NXy)C(=NXy)C(=NXy)C_6H_4X-2}Br(C-NXy)] (X = C(O)Me (**8a**), CN (**8b**)) were isolated (Scheme 2). A similar reaction from **3d** rendered an intractable complex mixture. It is worth noting that these reactions also require a nitrogen atmosphere; otherwise, as occurred in the reaction leading to **6a**,**b**, intractable mixtures form. One might believe that complexes **6** are intermediates in the formation of **8**. However, complexes **6** do not react with XyNC at room

Table 3. Details of Data Collection and Structure Refinement for the Complexes 11b, 12a, and 13b

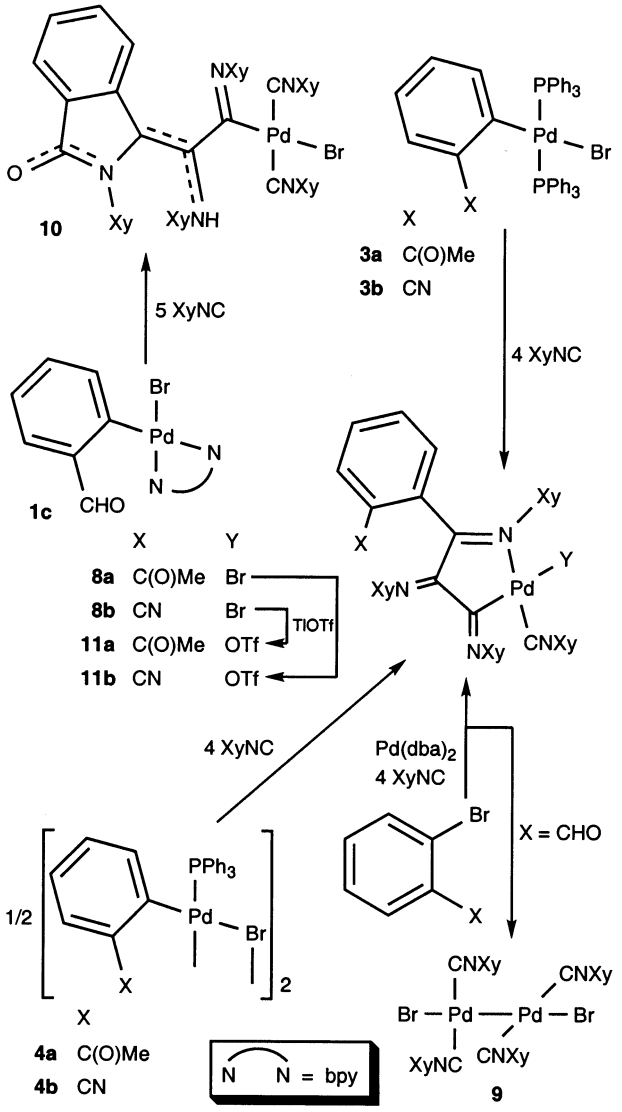
	11b	12a	13b
formula	$C_{44}H_{40}F_3N_5O_3PdS$	$C_{27}H_{24}F_3O_5PPdS$	$C_{76}H_{57}Br_2F_3N_3O_3P_3PdS$
cryst habit	red tablet	pale brown tablet	colorless tablet
cryst size (mm)	0.27 × 0.26 × 0.18	0.38 × 0.26 × 0.10	0.26 × 0.16 × 0.15
λ (Å)	0.710 73	0.710 73	0.710 73
cryst syst	orthorhombic	triclinic	monoclinic
space group	$Fdd2$	$P\bar{1}$	$P2_1/c$
a (Å)	30.842(2)	10.0477(8)	10.7914(8)
b (Å)	40.265(3)	11.0958(11)	24.809(2)
c (Å)	13.2880(10)	12.7645(11)	26.892(2)
α (deg)	90	93.101(3)	90
β (deg)	90	107.928(3)	100.357(3)
γ (deg)	90	94.628(3)	90
V (Å^3)	16 502	1344.9	7082.3
Z	16	2	4
ρ_{calcd} (Mg m^{-3})	1.421	1.617	1.614
M_r	882.27	654.89	1721.24
$F(000)$	7232	660	3416
T (°C)	−130	−140	−130
$2\theta_{max}$ (deg)	60	60	56.5
μ(Mo Kα) (mm^{-1})	0.56	0.88	2.0
abs cor	SADABS	SADABS	face indexing
transmissn	0.84−0.96	0.81−0.93	0.62−0.78
no. of rflns			
measd	84 492	25 576	138 945
unique	12 083	7811	17 567
R_{int}	0.051	0.020	0.098
R^a ($F > 4\sigma(F)$)	0.028	0.022	0.035
$R_w{}^b$ (F^2, all rflns)	0.061	0.061	0.069
no. of params	551	352	913
no. of restraints	474	1	800
S^c	0.99	1.07	0.95
max $\Delta\rho$ (e Å^{-3})	0.54	0.61	0.74

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

temperature. This suggests that the presence of PPh_3, as a product of the reaction between **3** or **4** and 4 equiv of XyNC, could be responsible for the change of reactivity of complexes **6** toward XyNC. It is possible that free PPh_3 coordinates in complexes **6**, forcing the insertion of the two isocyanide ligands (see Scheme 3). We have noted above that, in the absence of isocyanide, complexes **6** react with PPh_3 to give complex mixtures.

In addition, the transformation of **6a**,**b** into **8a**,**b** can be achieved by reaction with XyNC in a 1:1 molar ratio by heating the mixture in a closed tube in 1,2-dichloroethane at 90 °C overnight. **8a**,**b** could also be prepared by oxidative addition of the corresponding BrC_6H_4X-2 arenes to "Pd(dba)$_2$" in the presence of XyNC. When X was CH=CH$_2$ or CHO, the reactivity was again different. In the first case, the mixture decomposed to an ill-defined mixture, while in the second, the palladium(I) complex $[Pd_2Br_2(CNXy)_4]$ (**9**) formed. This complex has recently been prepared by reacting $[Pd_2(\mu\text{-}Br)_2(^tBu_3P)_2]$ with XyNC.[44] Our one-pot synthesis of **9** from "Pd(dba)$_2$" and BrC_6H_4CHO-2 is simpler and gives a similar yield. The previous preparations of complexes of this class involve comproportionation reactions between $[Pd(CNR)_n]$ and $[PdX_2(CNR)_2]$.[45−47] We have also prepared **9** by reacting $[Pd\{C_6H_3CH_2NH_2\text{-}2\text{-}X\text{-}5\}(\mu\text{-}Br)]_2$ (X = H, OMe, NO_2, F) with XyNC in a 1:6 molar ratio at room temperature.[14]

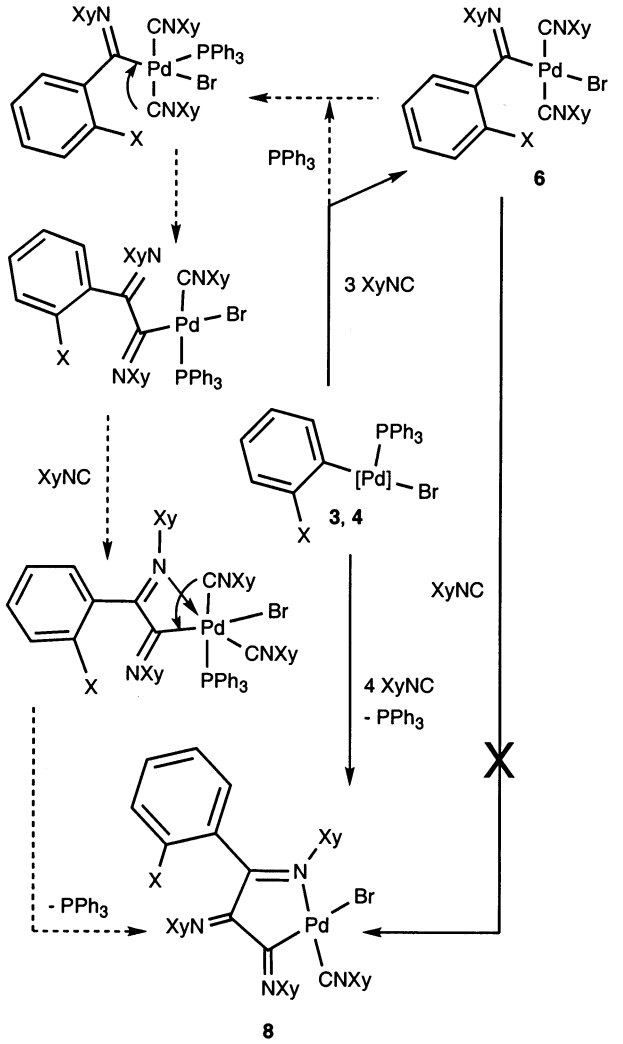
Scheme 2



A different behavior was observed in the case of the *o*-formylaryl complex **1c**, as its reaction with XyNC (1:5 molar ratio) in CH_2Cl_2 gave intractable mixtures. However, under nitrogen in acetone, complex **10** precipitated as a deep orange solid in 34% yield (Scheme 2). The values for carbon in many analyses of **10** were, like those of **5a**,**b**, somewhat lower than the calculated value (calcd C 65.93, found C 64.49), despite many attempts to purify the complex. Because H and N analyses were acceptable (calcd H 5.32, N 7.39; found H 5.18, N 7.22), the ^{1}H NMR spectrum did not show the presence of impurities, and its X-ray crystal structure was solved (single crystals of **10** were also analyzed), we believe that this disagreement between calculated and found carbon analyses is attributable to combustion problems of this compound. Workup of the mother liquors rendered a mixture for which ^{1}H NMR showed the presence of the Pd(I) dimer **9** and another

(45) Otsuka, S.; Tatsuno, Y.; Ataka, K. *J. Am. Chem. Soc.* **1971**, *93*, 6705.
(46) Rettig, M. F.; Kirk, E. A.; Maitlis, P. M. *J. Organomet. Chem.* **1976**, *111*, 113.
(47) Boehm, J. R.; Balch, A. L. *Inorg. Chem.* **1977**, *16*, 778.

Scheme 3



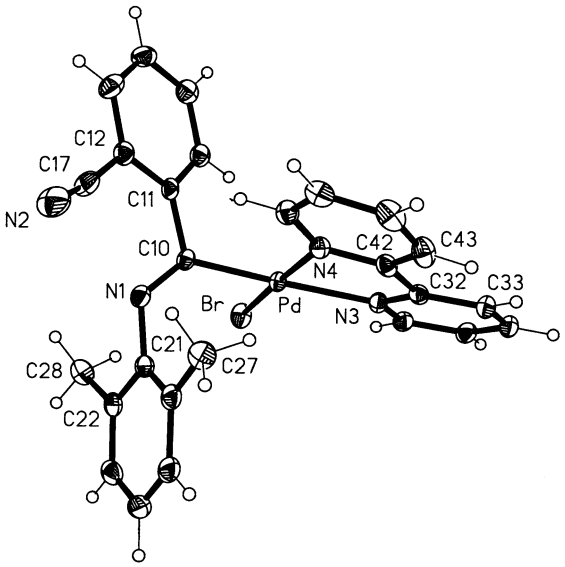
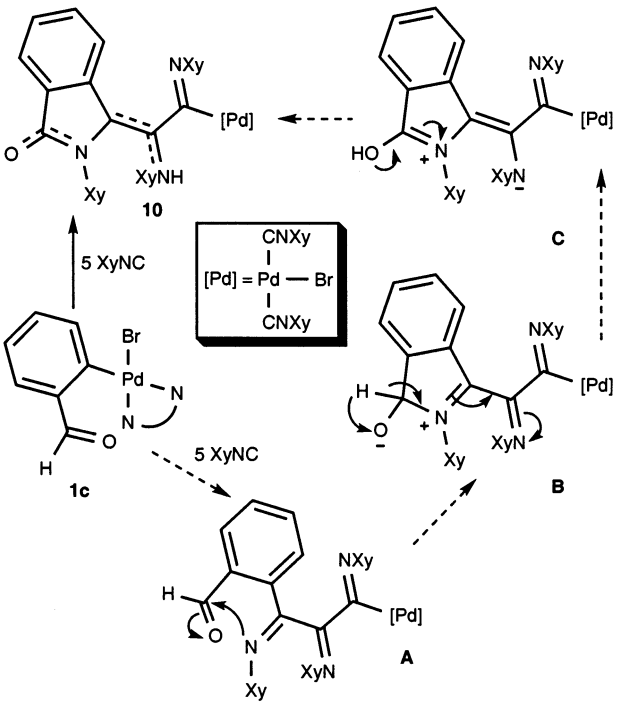
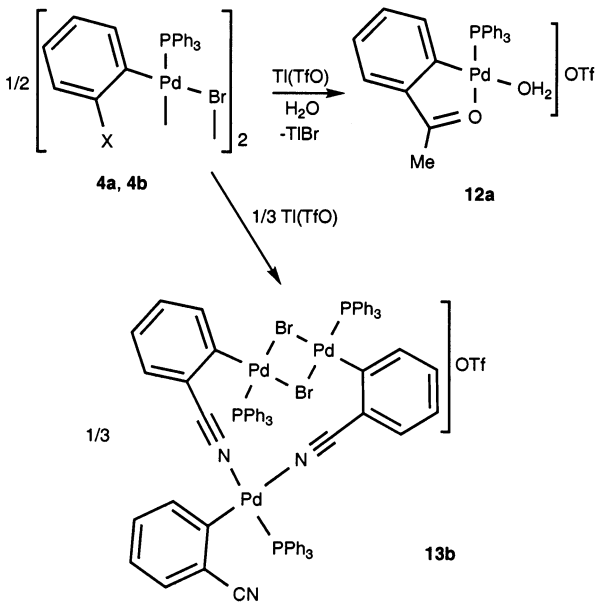


Figure 1. Thermal ellipsoid plot (50% probability level) of **5b**. Selected bond lengths (Å) and angles (deg): Pd−C(10) = 1.988(2), Pd−N(4) = 2.0655(18), Pd−N(3) = 2.1441(17), Pd−Br = 2.4259(3), N(1)−C(10) = 1.265(3), N(1)−C(21) = 1.418(3), N(2)−C(17) = 1.146(3), C(10)−C(11) = 1.499(3); C(10)−Pd−N(4) = 94.95(8), N(4)−Pd−N(3) = 78.44(7), C(10)−Pd−Br = 89.15(6), N(3)−Pd−Br = 97.50(5), C(10)−N(1)−C(21) = 126.33(19), N(1)−C(10)−C(11) = 117.05(18), N(1)−C(10)−Pd = 128.77(16), C(11)−C(10)−Pd = 113.93(14).

Scheme 4



Scheme 5



product similar to **10** that decomposed during attempts at chromatographic separation. The different behavior of **1c** may be due to the electrophilic nature of the carbon atom of the *o*-formyl substituent. We believe that the triinserted complex **A** (Scheme 4) could be an intermediate and that a nucleophilic attack at the formyl carbon of the nitrogen of the primarily inserted isocyanide could give the isoindole ring in **B**. In the case of the synthesis of **8** this nitrogen attacks at the metal center (Scheme 3). The intermediate **B** could evolve to **C**, bearing a carbon−carbon double bond, which, after an intermolecular proton migration from the OH group to the N of the second inserted isocyanide, could in turn lead to

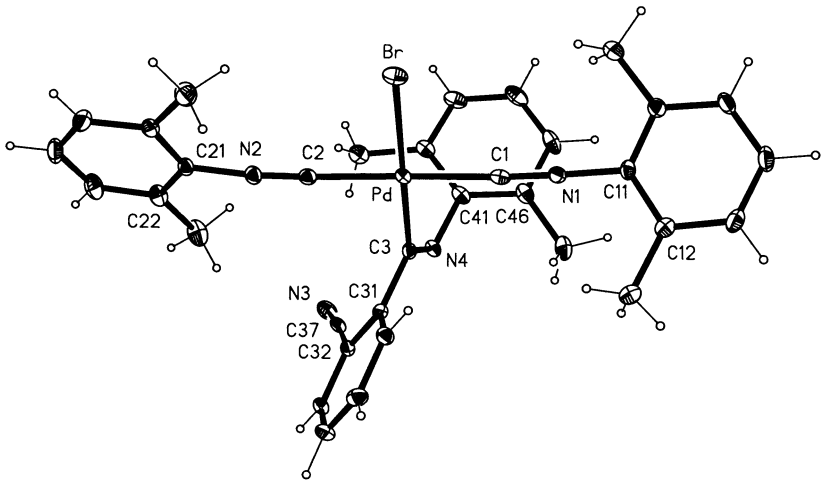


Figure 2. Thermal ellipsoid plot (30% probability level) of **6b**. Selected bond lengths (Å) and angles (deg): Pd−C(1) = 1.969(3), Pd−C(2) = 1.984(3), Pd−C(3) = 2.035(3), Pd−Br = 2.5333(5), C(1)−N(1) = 1.146(4), C(2)−N(2) = 1.146(4), C(3)−N(4) = 1.267(4), C(3)−C(31) = 1.477(4), C(11)−N(1) = 1.407(4), C(21)−N(2) = 1.405(4), C(37)−N(3) = 1.140(4), C(41)−N(4) = 1.426(4); C(1)−Pd−C(3) = 90.36(12), C(2)−Pd−C(3) = 88.14(12), C(1)−Pd−Br = 89.53(8), C(2)−Pd−Br = 91.98(8), N(1)−C(1)−Pd = 176.3(3), N(2)−C(2)−Pd = 178.0(3), N(4)−C(3)−C(31) = 118.0(3), N(4)−C(3)−Pd = 126.2(2), C(31)−C(3)−Pd = 115.8(2), C(1)−N(1)−C(11) = 178.2(3), C(2)−N(2)−C(21) = 172.1(3), C(3)−N(4)−C(41) = 121.9(3).

complex **10**. There is no precedent for this type of structure, which has been confirmed by an X-ray structure analysis. We have reported the synthesis of a highly functionalized ketenimine resulting after a di-insertion of XyNC in an (*o*-formylaryl)palladium complex. Its structure can be viewed as the result of a substitution of the [Pd]C{C(=NXy)C(NHXy)} group in **10** (see Scheme 4) by C=NXy.[13] The formation of such a ketenimine is also the result of the attack of the nitrogen of the primarily inserted isocyanide at the formyl carbon.

Reactivity of Complexes toward Tl(TfO). The ortho groups in the above complexes are able to coordinate intramolecularly to give cyclometalated complexes or intermolecularly to give polynuclear species. To force such coordination, we have carried out some reactions with Tl(TfO). Another objective of these reactions was to induce decomposition processes leading to N-heterocyclic compounds. However, whereas the first objective was attained in a few cases, no decompositions were observed. Thus, complexes **8a**,**b** react with Tl(TfO) to give complexes **11a**,**b**, resulting from substitution of the bromo ligand by triflate (Scheme 1). We have also studied the reactions of complexes **1**, **3**, and **4** with Tl(TfO). Although, most of our attempts gave intractable mixtures, positive results were obtained in two cases. Thus, the reaction of **4a** with Tl(TfO) gives a precipitate of TlBr and the cyclopalladated aquo complex [Pd{κ^2C,O-C_6H_4[C(O)Me]}(OH_2)(PPh_3)](TfO) (**12a**) (Scheme 5). The reaction is regioselective, since only the isomer with the aquo ligand trans to carbon was obtained (see discussion below).

The reaction of **4b** with Tl(TfO) led to the partial elimination of the bromo ligand (even if carried out with a 1:2 molar ratio) and the formation of the unusual trinuclear complex [Pd(C_6H_4CN-2)(κ^2N,N-**4b**)(PPh_3)](TfO) (**13b**). Its structure can be considered as the result of the coordination of **4b** as a chelating ligand, through the nitrogen atoms of the CN substituents, to a Pd(C_6H_4-CN-2)PPh_3 moiety. Two isomers, with the **4b** ligand in a cis or trans geometry, seem to be present in solution,

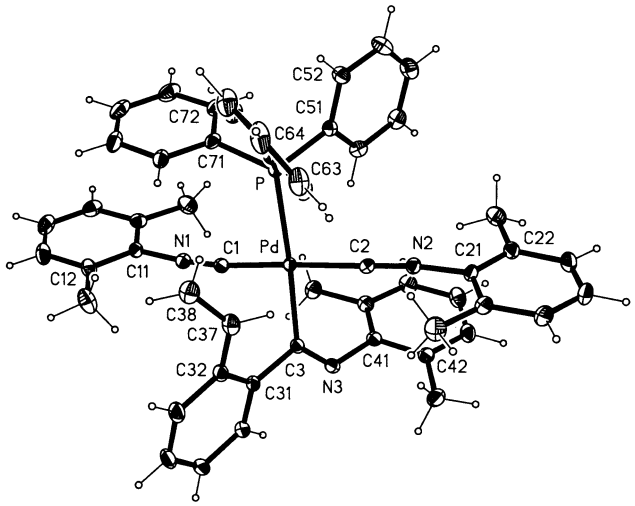


Figure 3. Thermal ellipsoid plot (30% probability level) of the cation of **7d**. Selected bond lengths (Å) and angles (deg): Pd−C(1) = 1.9875(18), Pd−C(2) = 1.9893(17), Pd−C(3) = 2.0726(18), Pd−P = 2.3991(5), C(1)−N(1) = 1.151-(2), C(2)−N(2) = 1.151(2), C(3)−N(3) = 1.259(2), C(3)−C(31) = 1.508(2), N(1)−C(11) = 1.405(2), N(2)−C(21) = 1.414(2), N(3)−C(41) = 1.414(2), S−O(1) = 1.420(3), S−O(2) = 1.435(3), S−O(3) = 1.438(2); C(1)−Pd−C(3) = 87.40(7), C(2)−Pd−C(3) = 88.57(7), C(1)−Pd−P = 91.10(5), C(2)−Pd−P = 93.53(5), N(1)−C(1)−Pd = 173.47(15), N(2)−C(2)−Pd = 178.16(16), N(3)−C(3)−C(31) = 117.38(17), N(3)−C(3)−Pd = 126.56(14), C(31)−C(3)−Pd = 115.97(12), C(1)−N(1)−C(11) = 171.89(18), C(2)−N(2)−C(21) = 172.96(18), C(3)−N(3)−C(41) = 126.64(16), O(1)−S−O(2) = 113.9(3), O(1)−S−O(3) = 116.1(2), O(2)−S−O(3) = 114.18(17).

in agreement with its ^{31}P NMR spectrum. However, only single crystals of the trans isomer could be obtained (see below).

Spectroscopic Properties of Complexes. The ν(C≡N) absorptions of complexes having coordinated XyNC and/or the aryl ligand C_6H_4CN-2 appear at 2248−2176 cm^{-1} (see Experimental Section). The assignments are difficult when both ligands are present in the same complex. However, by comparison between appropriate examples, it is possible to assign tentatively the lower

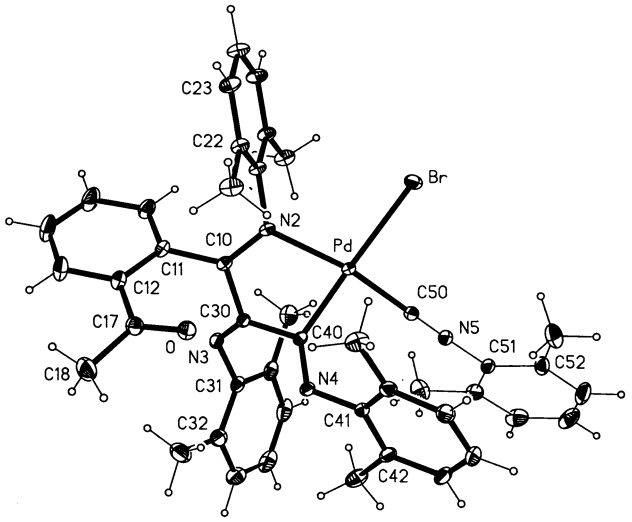


Figure 4. Thermal ellipsoid plot (30% probability level, solvent omitted) of **8a**·$^1/_2CH_2Cl_2$. Selected bond lengths (Å) and angles (deg): Pd−C(50) = 1.9327(16), Pd−C(40) = 1.9936(15), Pd−N(2) = 2.1243(12), Pd−Br = 2.5390(2), N(2)−C(10) = 1.2908(19), N(2)−C(21) = 1.4491(18), N(3)−C(30) = 1.2704(19), N(3)−C(31) = 1.4198(19), N(4)−C(40) = 1.2624(19), N(4)−C(41) = 1.415(2), N(5)−C(50) = 1.150-(2), N(5)−C(51) = 1.3949(19), O−C(17) = 1.217(2), C(10)−C(11) = 1.489(2), C(10)−C(30) = 1.496(2), C(30)−C(40) = 1.492(2); C(50)−Pd−C(40) = 90.54(6), C(40)−Pd−N(2) = 80.72(5), C(50)−Pd−Br = 89.47(4), N(2)−Pd−Br = 100.23-(3), C(10)−N(2)−C(21) = 120.62(13), C(10)−N(2)−Pd = 113.57(10), C(21)−N(2)−Pd = 125.28(10), C(30)−N(3)−C(31) = 121.78(13), C(40)−N(4)−C(41) = 122.88(13), C(50)−N(5)−C(51) = 177.04(16), N(2)−C(10)−C(11) = 128.14(14), N(2)−C(10)−C(30) = 112.90(13), C(11)−C(10)−C(30) = 118.17(13), O−C(17)−C(12) = 120.44(15), O−C(17)−C(18) = 120.11(17), C(12)−C(17)−C(18) = 119.45(16), N(3)−C(30)−C(40) = 128.68(13), N(3)−C(30)−C(10) = 117.12(13), C(40)−C(30)−C(10) = 112.92(12), N(4)−C(40)−C(30) = 120.27(13), N(4)−C(40)−Pd = 134.44(11), C(30)−C(40)−Pd = 105.01(10), N(5)−C(50)−Pd = 172.59(14).

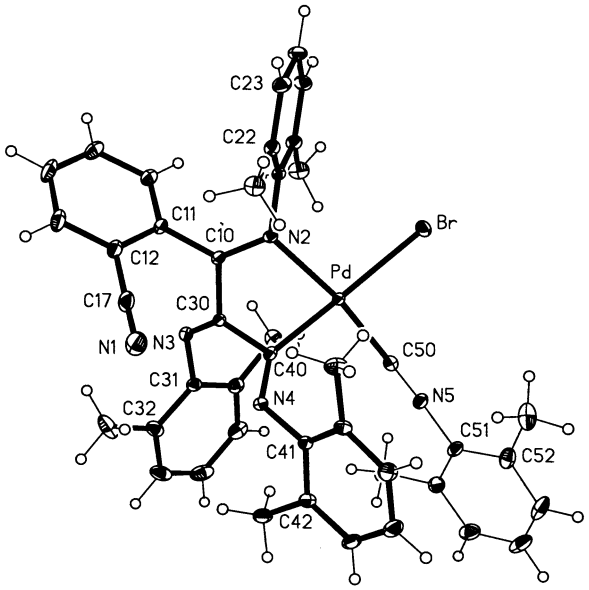


Figure 5. Thermal ellipsoid plot (30% probability level, solvent omitted) of **8b**·$^1/_2CH_2Cl_2$. Selected bond lengths (Å) and angles (deg): Pd−C(50) = 1.9386(19), Pd−C(40) = 2.0037(18), Pd−N(2) = 2.1174(14), Pd−Br = 2.5282(3), C(10)−N(2) = 1.288(2), C(10)−C(11) = 1.485(2), C(10)−C(30) = 1.496(2), C(17)−N(1) = 1.142(3), C(21)−N(2) = 1.450(2), C(30)−N(3) = 1.265(2), C(30)−C(40) = 1.504(2), C(31)−N(3) = 1.423(2), C(40)−N(4) = 1.258(2), C(41)−N(4) = 1.422(2), C(50)−N(5) = 1.149(2), C(51)−N(5) = 1.399-(2); C(50)−Pd−C(40) = 91.17(7), C(40)−Pd−N(2) = 80.71-(6), C(50)−Pd−Br = 90.38(5), N(2)−Pd−Br = 97.89(4), N(2)−C(10)−C(11) = 127.23(16), N(2)−C(10)−C(30) = 113.21(15), C(11)−C(10)−C(30) = 119.55(15), N(1)−C(17)−C(12) = 178.4(3), N(3)−C(30)−C(10) = 117.68(15), N(3)−C(30)−C(40) = 129.30(16), C(10)−C(30)−C(40) = 112.04-(15), N(4)−C(40)−C(30) = 118.44(15), N(4)−C(40)−Pd = 136.71(13), C(30)−C(40)−Pd = 104.55(11), N(5)−C(50)−Pd = 178.27(17), C(10)−N(2)−C(21) = 120.54(14), C(10)−N(2)−Pd = 113.77(11), C(21)−N(2)−Pd = 125.54(11), C(30)−N(3)−C(31) = 121.28(15), C(40)−N(4)−C(41) = 125.29(15), C(50)−N(5)−C(51) = 175.30(19).

frequencies to the coordinated isocyanides and the higher ones to the nitrile substituents. Thus, the coordinated XyNC ligands appear within the range 2176−2210 cm^{-1} and the nitrile groups at 2214−2226 cm^{-1}. In the case of complex **13b**, in which two nitrile substituents are coordinated to a palladium atom, a shift to a higher frequency (2248 cm^{-1}) is observed; a shoulder band at 2214 cm^{-1} is assigned to the uncoordinated CN. The ν(C═O) absorptions of the acetylaryl complexes **5a**, **6a**, **8a**, and **11a** appear at 1630−1700 cm^{-1}. In the case of the cyclopalladated complex **12a** this band shifts to lower frequency (1582 cm^{-1}) because of the coordination of the carbonyl oxygen to the palladium atom, as previously observed in related C,O palladacycles.[8,13,15,16]

The ^{1}H NMR spectra of complexes **6** and **7d** show one singlet for the two methyl groups of the inserted XyNC and another one for the four methyls of the two equivalent coordinated isocyanides. In **5a**, the methyl substituents of the inserted XyNC give a broad signal, suggesting a slow rotation of the Xy group. In complex **10** the presence of four methyl singlets, one of them with an integrated intensity twice that of the others, indicates also a trans geometry and free rotation of the Xy groups. In contrast, complexes **8** and **11** show six singlets, each corresponding to a methyl group, and another one integrated to two methyls; this suggests a steric hindrance of the rotation of three of the xylyl groups, while the fourth one rotates freely.

The ^{31}P NMR spectrum of **13b** shows two sets of signals, each corresponding to an AB system and a singlet. We believe that this is due to the existence of **13b** in solution as a mixture of complexes derived from *cis*-**4b** and *trans*-**4b**.

Structure of Complexes. We have shown that the following pairs of ligands have increasing phobia of being mutually trans in palladium(II) complexes: X-donor/Y-donor (X, Y = halogen, N-donor, P-donor) ≈ C-donor/X-donor (X = halogen, N-donor) < C-donor/P-donor < C-donor/C-donor. The antisymbiotic effect[48] does not explain these differences. This effect assumes that two soft ligands in mutually trans positions will have a destabilizing effect on each other when attached to a class b metal such as Pd(II). However, Pd(II) complexes with pairs of soft ligands such as PR_3/PR_3, Br/Br, and Br/PR_3 in mutually trans positions are very stable, while others, also with soft ligands, such as C-donor/P-donor and C-donor/C-donor, are not. In ad-

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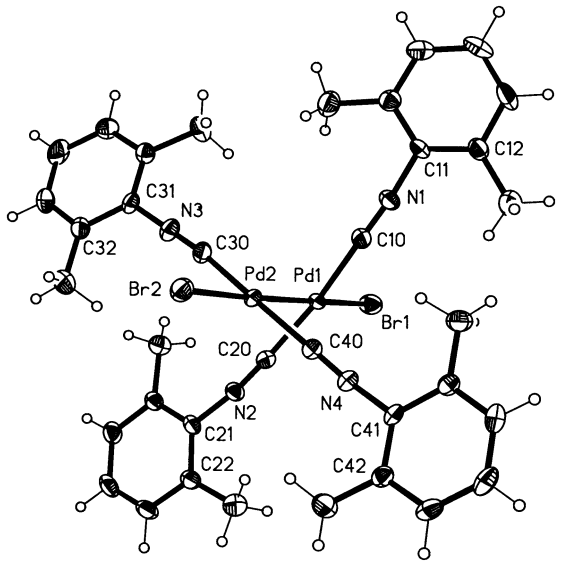

Figure 6. Thermal ellipsoid plot (50% probability level) of **9**. Selected bond lengths (Å) and angles (deg): Pd(1)−C(20) = 1.957(2), Pd(1)−C(10) = 1.966(2), Pd(1)−Br(1) = 2.5193(3), Pd(1)−Pd(2) = 2.5269(3), Pd(2)−C(40) = 1.956(2), Pd(2)−C(30) = 1.963(2), Pd(2)−Br(2) = 2.5294(3), N(1)−C(10) = 1.153(2), N(1)−C(11) = 1.410(2), N(2)−C(20) = 1.151(2), N(2)−C(21) = 1.408(2), N(3)−C(30) = 1.155(2), N(3)−C(31) = 1.405(2), N(4)−C(40) = 1.161(2), N(4)−C(41) = 1.406(2); C(20)−Pd(1)−C(10) = 170.78(8), C(40)−Pd(2)−C(30) = 170.07(8), C(20)−Pd(1)−Br(1) = 97.02(6), C(10)−Pd(1)−Br(1) = 91.89(6), C(20)−Pd(1)−Pd(2) = 80.62(6), C(10)−Pd(1)−Pd(2) = 90.36(6), C(40)−Pd(2)−Pd(1) = 83.23(6), C(30)−Pd(2)−Pd(1) = 87.33(6), C(40)−Pd(2)−Br(2) = 98.41(6), C(30)−Pd(2)−Br(2) = 91.12(6), C(10)−N(1)−C(11) = 171.8(2), C(20)−N(2)−C(21) = 172.3(2), C(30)−N(3)−C(31) = 178.8(2), C(40)−N(4)−C(41) = 172.9(2), N(1)−C(10)−Pd(1) = 173.41(18), N(2)−C(20)−Pd(1) = 177.30(18), N(3)−C(30)−Pd(2) = 174.24(18), N(4)−C(40)−Pd(2) = 178.89(18).

dition, this destabilizing effect depends on the class b metal involved. It is generally less marked for Pt(II) than for Pd(II). We have named this destabilizing effect transphobia (*T*), a term that has already been accepted by many authors.[19−21,49−54] When the product of a reaction contains a pair of ligands with high *T* in trans positions, one of which is generally a C-donor, a further reaction such as an X−Y coupling process (X = C, Y = C, N, O, P),[2,20,49,55,56] an insertion of atmospheric O_2 into the C−Pd bond,[19,20] or an intramolecular redox reaction usually takes place.[57,58] In contrast, if the two pairs of trans ligands have low *T*, the reaction product tends to be stable. Although the observation of the geometries of stable complexes cannot always provide information on the degree of *T* of their possible pairs of trans ligands, we think that looking at the geometry of a family of complexes would allow more members to be placed in the scale of *T*. Thus, the trans geometry of complexes **6a**,**b**,**d**, **7d**, and **10** could be a result of the relationship *T*[XyNC/CNXy] < *T*[XyNC/C(=NXy)R] (R = C_6H_4X-2, X = C(O)Me, CN, CH=CH_2). We have recently reported the complexes $[PdX\{C(=E)R\}(CNR')_2]^{n+}$ (X = Br, I, PPh_3; E = O, NXy, N^{t}Bu; R = C_6H_3Y-2-Z-5 (Y = NH_2, OH, OC(O)Me; Z = H, NO_2); *n* = 0, 1),[21,22] which also have a trans geometry. However, the differing steric requirements of the ligands involved could also play a significant role in determining the geometry of these complexes. We have reported that two complexes analogous to **7d**, *trans*-[Pd{C(=N^{t}Bu)$C_6H_4NH_2$-2-X-5}(CN^t-Bu)$_2$(PPh_3)](TfO) (X = H, NO_2), decompose to give the

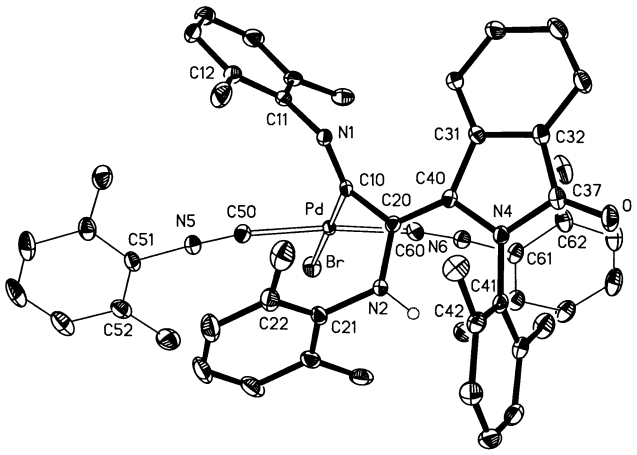

Figure 7. Thermal ellipsoid plot (30% probability level, solvent omitted) of **10**·CH_2Cl_2. Hydrogen atoms, except that attached to N(2), have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−C(50) = 1.986(3), Pd−C(60) = 1.999(3), Pd−C(10) = 2.031(3), Pd−Br = 2.5288(4), O−C(37) = 1.220(3), N(1)−C(10) = 1.267(3), N(1)−C(11) = 1.413(4), N(2)−C(20) = 1.378(3), N(2)−C(21) = 1.426(3), N(4)−C(37) = 1.384(4), N(4)−C(40) = 1.439(3), N(4)−C(41) = 1.440(3), N(5)−C(50) = 1.150(4), N(5)−C(51) = 1.410(3), N(6)−C(60) = 1.151(4), N(6)−C(61) = 1.408(4), C(10)−C(20) = 1.503(4), C(20)−C(40) = 1.368(4), C(31)−C(40) = 1.476(4), C(32)−C(37) = 1.459(4); C(50)−Pd−C(10) = 93.09(11), C(60)−Pd−C(10) = 90.64(11), C(50)−Pd−Br = 88.25(9), C(60)−Pd−Br = 88.30(8), C(10)−N(1)−C(11) = 127.9(3), C(20)−N(2)−C(21) = 125.8(2), C(37)−N(4)−C(40) = 112.3(2), C(37)−N(4)−C(41) = 119.7(2), C(40)−N(4)−C(41) = 127.9(2), C(50)−N(5)−C(51) = 174.5(3), C(60)−N(6)−C(61) = 173.7(3), N(1)−C(10)−C(20) = 119.3(3), N(1)−C(10)−Pd = 127.7(2), C(20)−C(10)−Pd = 112.93(17), O−C(37)−N(4) = 124.7(3), O−C(37)−C(32) = 129.8(3), N(4)−C(37)−C(32) = 105.5(2), C(20)−C(40)−N(4) = 123.6(2), C(20)−C(40)−C(31) = 131.4(3), N(4)−C(40)−C(31) = 104.7(2), N(5)−C(50)−Pd = 169.3(3), N(6)−C(60)−Pd = 171.9(3).

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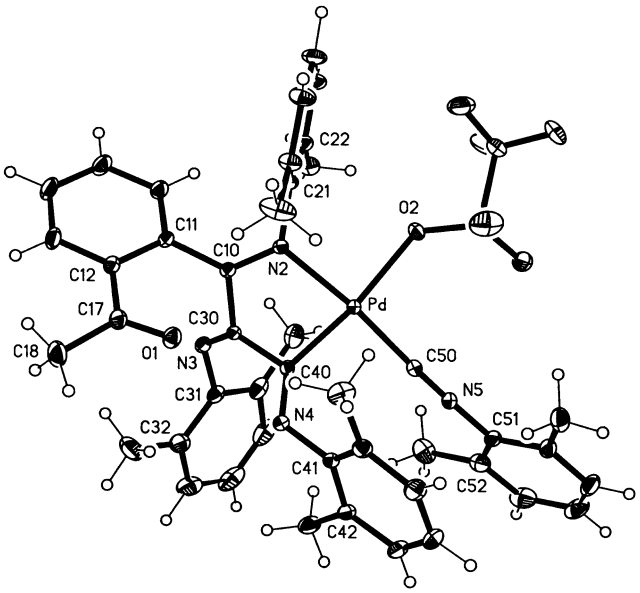

Figure 8. Thermal ellipsoid plot (30% probability level, solvent omitted) of **11a**·$^1/_2$$CHCl_3$. Selected bond lengths (Å) and angles (deg): Pd−C(50) = 1.959(2), Pd−C(40) = 1.9772(19), Pd−N(2) = 2.0935(16), Pd−O(2) = 2.1678(15), N(2)−C(10) = 1.283(3), N(2)−C(21) = 1.444(2), N(3)−C(30) = 1.268(3), N(3)−C(31) = 1.425(3), N(4)−C(40) = 1.252(2), N(4)−C(41) = 1.420(3), N(5)−C(50) = 1.147(3), N(5)−C(51) = 1.398(3), O(1)−C(17) = 1.221(3), C(10)−C(11) = 1.491(3), C(10)−C(30) = 1.496(3), C(12)−C(17) = 1.486(3), C(30)−C(40) = 1.508(3), S−O(3) = 1.423(2), S−O(4) = 1.428(2), S−O(2) = 1.4559(17); C(50)−Pd−C(40) = 92.71(8), C(40)−Pd−N(2) = 81.56(7), C(50)−Pd−O(2) = 94.25(8), N(2)−Pd−O(2) = 91.16(6), C(10)−N(2)−C(21) = 123.98(17), C(10)−N(2)−Pd = 113.92(13), C(21)−N(2)−Pd = 121.87(13), C(30)−N(3)−C(31) = 121.28(18), C(40)−N(4)−C(41) = 123.52(18), C(50)−N(5)−C(51) = 178.1(2), N(2)−C(10)−C(11) = 128.62(18), N(2)−C(10)−C(30) = 111.89(17), C(11)−C(10)−C(30) = 118.81(17), N(3)−C(30)−C(10) = 117.93(17), N(3)−C(30)−C(40) = 128.39(17), C(10)−C(30)−C(40) = 112.49(16), N(4)−C(40)−C(30) = 120.86(18), N(4)−C(40)−Pd = 136.12(16), C(30)−C(40)−Pd = 102.93(12), O(3)−S−O(4) = 117.51(15), O(3)−S−O(2) = 113.61(14), O(4)−S−O(2) = 113.67(13).

Pd(I) complex $[Pd_2(PPh_3)_2(CNXy)_4](TfO)_2$ as a consequence of the high *T*[Ph_3P/C(=N^{t}Bu)$C_6H_4NH_2$-2-X-5] = T_1. The stability of **7d** could mean that T_1 > *T*[Ph_3P/C(=NXy)C_6H_4CH=CH_2-2]. The cis disposition of both C-donor ligands in **8a**,**b** and **11a**,**b** or of PPh_3 and the aryl ligand in **12a** is consistent with the large *T*[C-donor/C-donor] or *T*[C-donor/P-donor], respectively.

X-ray Crystal Structures. The molecular structures of **5b** (Figure 1), **6b** (Figure 2), **7d** (Figure 3), **8a**·$^1/_2$-CH_2Cl_2 (Figure 4), **8b**·$^1/_2$$CH_2Cl_2$ (Figure 5), **9** (Figure 6), **10**·CH_2Cl_2 (Figure 7), **11a**·$^1/_2$$CHCl_3$ (Figure 8), **11b** (Figure 9), **12a** (Figure 10), and **13b** (Figure 11) have been determined by X-ray diffraction studies. The Pd−C bond distances of the iminoacyl ligands decrease, in agreement with the decreasing trans influence of the ligand L located in the trans position. Thus, these values are as follows (in Å): 2.0726(18) (**7d**; L = PPh_3) > 2.035(3)−1.983(3) (**6b**, **8a**,**b**, **10**, **13b**; L = Br) ≈ 1.992(3) (**13b**; L = ArCN) ≳ 1.988(2) (**5b**; L = bpy) = 1.9772(19)−1.9681(18) (**11a**, **11b**; L = OTf). The Pd−Br distances also allow us to correlate longer distances with greater trans influence. Thus, the order is as follows (in Å):

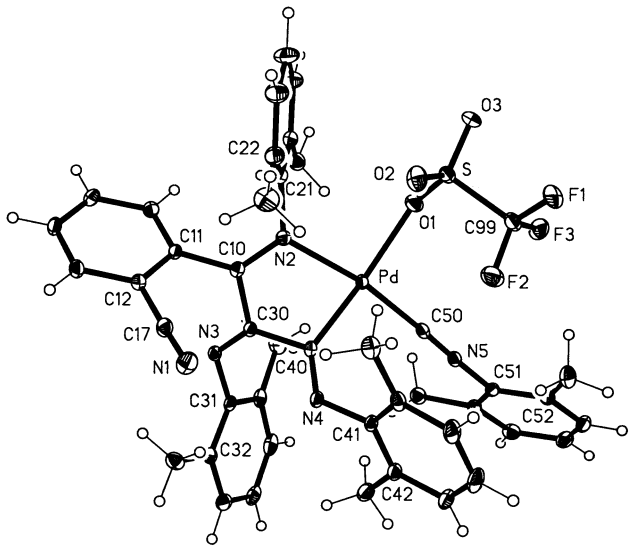

Figure 9. Thermal ellipsoid plot (30% probability level) of **11b**. Only one position of the disordered triflate is shown. Selected bond lengths (Å) and angles (deg): Pd−C(50) = 1.9619(19), Pd−C(40) = 1.9681(18), Pd−N(2) = 2.1086(15), Pd−O(1) = 2.1894(15), N(1)−C(17) = 1.144(3), N(2)−C(10) = 1.291(2), N(2)−C(21) = 1.449(2), N(3)−C(30) = 1.268(2), N(3)−C(31) = 1.438(2), N(4)−C(40) = 1.255(2), N(4)−C(41) = 1.421(2), N(5)−C(50) = 1.154(2), N(5)−C(51) = 1.407(2), C(10)−C(11) = 1.483(2), C(10)−C(30) = 1.495(3), C(12)−C(17) = 1.447(3), C(30)−C(40) = 1.513(2), O(1)−S = 1.4381(17), S−O(3) = 1.431(3), S−O(2) = 1.435(2); C(50)−Pd−C(40) = 90.62(7), C(40)−Pd−N(2) = 81.01(7), C(50)−Pd−O(1) = 95.32(7), N(2)−Pd−O(1) = 93.81(6), C(10)−N(2)−C(21) = 122.84(16), C(10)−N(2)−Pd = 113.93(12), C(21)−N(2)−Pd = 123.18(12), C(30)−N(3)−C(31) = 120.53(15), C(40)−N(4)−C(41) = 125.34(16), C(50)−N(5)−C(51) = 176.12(19), N(2)−C(10)−C(11) = 127.25(17), N(2)−C(10)−C(30) = 114.12(16), C(11)−C(10)−C(30) = 118.62(15), N(3)−C(30)−C(10) = 119.35(16), N(3)−C(30)−C(40) = 128.99(17), C(10)−C(30)−C(40) = 111.39(15), N(4)−C(40)−C(30) = 118.56(16), N(4)−C(40)−Pd = 133.29(14), C(30)−C(40)−Pd = 107.18(12), N(5)−C(50)−Pd = 173.43(16), O(3)−S−O(2) = 118.3(2), O(3)−S−O(1) = 114.46(19), O(2)−S−O(1) = 110.98(13).

2.5469(4)−2.5451(4) (**13b**; aryl) > 2.5333(5)−2.5282(3) (**6b**, **8a**,**b**, **10**; L = C(=NAr)Xy) > 2.5204(4)−2.4963(4) (**13b**; PPh_3) > 2.4259(3) (**5b**; L = bpy). Similarly, the Pd−N bond distances in **5b** (Pd−N(4), 2.0655(18) Å; Pd−N(3), 2.1441(17) Å) show the greater trans influence of the C-donor iminoacyl ligand with respect to the bromo ligand. Looking at these scales, our proposal that the transphobia could be directly related to the trans influence is reinforced.[50] Under this assumption, two ligands with great trans influence will suffer a great transphobia.

The structure of the Pd(I) dimer **9** (Figure 6) is similar to that of the few crystal structures reported of related complexes $[Pd_2(CNR)_4L_2]^{n+}$: R = Me, L = MeNC, *n* = 2,[59] L = I, *n* = 0;[60] R = ^{t}Bu, L = PPh_3, *n* = 2,[21] L = Cl, *n* = 0.[61,62] **9** contains two directly bonded Pd atoms, each having two coordinated isocyanides in trans positions

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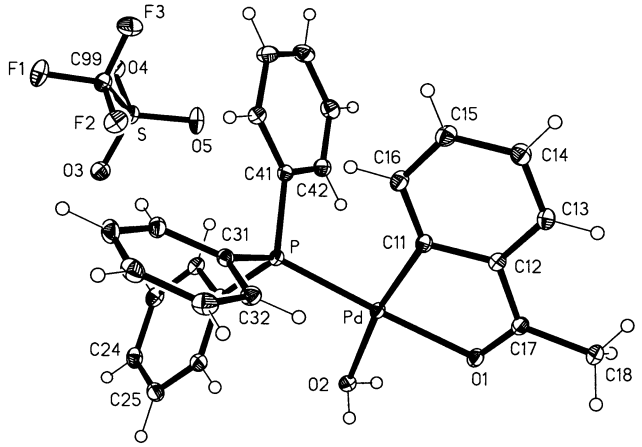

Figure 10. Thermal ellipsoid plot (50% probability level) of **12a**. Selected bond lengths (Å) and angles (deg): Pd−C(11) = 1.9838(13), Pd−O(1) = 2.1045(10), Pd−O(2) = 2.1373(10), Pd−P = 2.2268(4), O(1)−C(17) = 1.2521(17), S−O(3) = 1.4375(12), S−O(4) = 1.4410(12), S−O(5) = 1.4442(12); C(11)−Pd−O(1) = 81.91(5), O(1)−Pd−O(2) = 88.79(4), C(11)−Pd−P = 95.32(4), O(2)−Pd−P = 93.98(3), O(3)−S−O(4) = 114.95(8), O(3)−S−O(5) = 114.27(8), O(4)−S−O(5) = 115.86(8).

and a bromo ligand in the axial position. The angle between the two coordination planes is 84°. The distance between both palladium atoms (2.5269(3) Å) is the shortest reported (published range 2.5310(9)−2.5596(7) Å). The Pd−C bond distances in **9** (1.966(2)−1.956(2) Å) are shorter than those in the Pd(II) complexes **6b**, **7d**, and **10**, also containing mutually trans XyNC ligands (range 1.999(3)−1.984(3) Å), although the Pd−C(1) distance in **6b** (1.969(3) Å) is significantly below this range. However, the C≡N bond distances are similar for the above four complexes (range 1.161(2)−1.146(4) Å), suggesting that the differences in Pd−C bond distances are due to the different Pd−C σ bond strengths and that the Pd−C π bond is probably negligible in both groups of complexes. The C−N−C angle of the isocyanides deviate slightly from linearity (range 178.8(2)−171.89(18)°), supporting the proposal of slight, if any, π-character of the Pd−C bond.

The [Pd]C═NXy bond distances of the iminoacyl ligands in complexes **5b**, **6b**, **7d**, **8a**,**b**, **10**, and **11a**,**b** are in the range 1.267(3)−1.252(2) Å. In the triinserted complexes **8** and **11**, the C═N distances corresponding to the second inserted molecule of XyNC are in the upper limit of the above range (N(3)−C(30) = 1.2704(19)−1.265(2) Å). All these lengths are as expected for a C═N bond (the mean value for C(aryl)−C═NR distances is 1.279 Å).[63] The (aryl)C═N(Xy)[Pd] distances corresponding to the third inserted molecule of XyNC in **8** and **11** are significantly longer than the other two (N(2)−C(10) = 1.291(2)−1.283(3) Å) as a result of the coordination of the nitrogen atom to Pd. In the triinserted complex **10**, the HN(2)−C(20) bond length (1.378(3) Å), corresponding to the second inserted isocyanide, is intermediate between the above C═N distances and that of the C(21)−N(2) bond (1.426(3) Å). This fact, the wide C(21)−N(2)−C(20) angle (125.8(2)°), and the short C(20)−C(40) bond (1.368(4) Å), compared with C(31)−C(40) (1.476(4) Å), suggest a delocalization of π electron density around the N(2)−C(20)−C(40) group. Similarly, the angles around N(4) (112.3(2), 119.7(2), and 127.9(2)°) and the short N(4)−C(37) bond distance (1.384(4) Å) compared with those of N(4)−C(40) (1.439(3) Å) and N(4)−C(41) (1.440(3) Å) also point to a delocalization of π electron density along the N(4)−C(37)−O moiety. The atoms C(31−36)−C40−C(20)−C(10)−N(2)−C(21)−N(4)−C(41)−C37−O are almost coplanar. Some deviations are as follows (in Å): C(20), 0.12; C(10), 0.22; N(2), 0.33; C(21), 0.04; C(41), 0.08.

Despite the structural similarity of the triflato complexes **11a** (Figure 8) and **11b** (Figure 9), the Pd−O

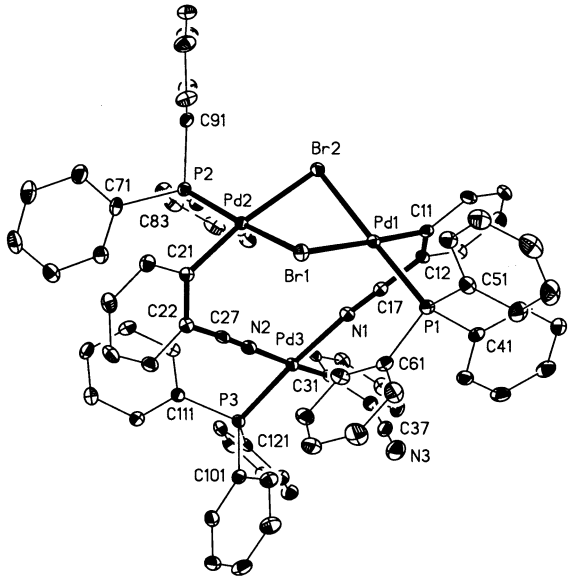

Figure 11. Thermal ellipsoid plot (30% probability level) of **13b**. Hydrogen atoms, the anion, and the minor disorder component of the C31−N3 ring are omitted. Selected bond lengths (Å) and angles (deg): Pd(1)−C(11) = 1.993(3), Pd(2)−C(21) = 1.983(3), Pd(3)−C(31) = 1.992(3), Pd(1)−P(1) = 2.2609(8), Pd(2)−P(2) = 2.2516(8), Pd(3)−P(3) = 2.2522(8), Pd(1)−Br(2) = 2.5204(4), Pd(1)−Br(1) = 2.5469(4), Pd(2)−Br(1) = 2.4963(4), Pd(2)−Br(2) = 2.5451(4), Pd(3)−N(1) = 2.088(2), Pd(3)−N(2) = 2.102(3), N(1)−C(17) = 1.144(3), N(2)−C(27) = 1.141(4), S−O(1) = 1.424(4), S−O(3) = 1.427(3), S−O(2) = 1.439(3); C(11)−Pd(1)−P(1) = 87.96(8), C(11)−Pd(1)−Br(2) = 91.61(8), P(1)−Pd(1)−Br(1) = 93.39(2), Br(2)−Pd(1)−Br(1) = 87.022(12), C(21)−Pd(2)−P(2) = 89.87(8), C(21)−Pd(2)−Br(1) = 88.83(8), P(2)−Pd(2)−Br(2) = 94.84(2), Br(1)−Pd(2)−Br(2) = 87.578(12), C(31)−Pd(3)−N(1) = 88.30(11), N(1)−Pd(3)−N(2) = 91.39(9), C(31)−Pd(3)−P(3) = 88.36(9), N(2)−Pd(3)−P(3) = 92.12(7), Pd(2)−Br(1)−Pd(1) = 83.789(12), Pd(1)−Br(2)−Pd(2) = 83.341(11), C(27)−N(2)−Pd(3) = 176.9(3), N(2)−C(27)−C(22) = 177.4(3), C(17)−N(1)−Pd(3) = 174.7(2), N(1)−C(17)−C(12) = 178.7(3), O(1)−S−O(3) = 115.7(3), O(1)−S−O(2) = 114.2(3), O(3)−S−O(2) = 114.9(2).

Table 4. Hydrogen Bonds for Complex 12a[a]

	D−H···A	D−H	H···A	D···A
O(2)−H(01)···O(5)#1	0.785(16)	1.897(17)	2.6643(16)	165(2)
O(2)−H(02)···O(4)#2	0.781(16)	2.110(17)	2.7521(16)	139.7(19)
O(2)−H(02)···O(1)#3	0.781(16)	2.394(18)	2.9674(14)	131.2(18)
C(13)−H(13)···O(3)#4	0.95	2.36	3.3097(19)	173.3
C(18)−H(18B)···O(3)#4	0.98	2.51	3.4874(19)	172.3
C(23)−H(23)···O(3)	0.95	2.57	3.305(2)	134.5
C(26)−H(26)···O(4)#2	0.95	2.62	3.4712(19)	148.7

[a] Distances are given in Å and angles in deg. Symmetry transformations used to generate equivalent atoms: (#1) $-x+1, -y+1, -z+1$; (#2) $x, y+1, z$; (#3) $-x+1, -y+2, -z+1$; (#4) $x+1, y+1, z$.

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bond distances are different (2.1678(15) and 2.1894(15) Å, respectively). However, the triflate in **11b** is disordered over two positions with occupancies of ca. 2:1 and the Pd−O(1) distance should not be regarded as very reliable. The Pd−OTf distance seems to be very sensitive to small changes in the nature of the trans ligand. Thus, in the crystal structures of triflato complexes in which this ligand is trans to a C-donor ligand, the values of the Pd−O bond are in the wide range of 2.271(7)−2.126(5) Å.[17,50,64−66]

In complex **12a**, the phosphine and aryl ligands are mutually cis, in agreement with the strong transphobia of these ligands. The coordination of the oxygen of the carbonyl group is responsible for the lengthening of the C−O bond (1.2521(17) Å) with respect to that in **8a** (1.217(2) Å) or **11a** (1.221(3) Å) and a shifting to lower frequencies of the ν(C═O) band in its IR spectrum (see above) with respect to those in the other complexes containing the uncoordinated 2-acetylphenyl group (**5a**, **6a**, **8a**, and **11a**). The packing of compound **12a** involves several hydrogen bonds of the types O−H···O and C−H···O (see Table 4). Two formula units form a centrosymmetric dimer through hydrogen bonds O(2)−H(01)···O(5) and the three-center O(2)−H(02)···O(4)/O(1). This dimeric structure is supported by the "weak" hydrogen bond C(26)H(26)···O(4) (H···O = 2.62 Å). The dimers link to give a unidimensional polymer parallel to the *x* axis via the bifurcate system C(13)−H(13)···O(3)···H(18)−C(18) hydrogen bonds (H···O = 2.36, 2.51 Å). Finally, these polymeric units link to give a layer parallel to the *xz* plane through O(3)···H(23)−C(23) hydrogen bonds (H···O = 2.57 Å).

The structure of the cation of **13b** consists of a *trans*-**4b** molecule coordinated through the nitrogen atoms of both nitrile substituents to a *cis*-Pd(C_6H_4CN-2)(PPh_3) fragment (Figure 11). The molecular planes of Pd(1) and Pd(2) (the dimeric unit) are folded, forming an angle of 40° associated with the coordination to Pd(3); note, however, that the coordination at Pd(2) is far from planar, with Br(2) lying 0.60 Å out of the plane of the other four atoms. The coordination of the two nitrile groups does not affect their C≡N distances, since they are very similar to that shown by the uncoordinated nitrile (C(27)−N(2), 1.141(4) Å; C(17)−N(1), 1.144(3) Å; C(37)−N(3), 1.139(5) Å).

Conclusions

2-R-arylpalladium(II) complexes containing the ligand bpy react with XyNC to give monoinserted complexes when the ortho substituent R is C(O)Me, CN (1:1 and 1:3 molar ratios), or CH═CH_2 (1:3 molar ratio). When the molar ratio was 1:1 and R = C(O)Me, CN, the corresponding monoinserted complex containing bpy was isolated. When the molar ratio was 1:3 and R = C(O)Me, CN, CH═CH_2 monoinsertion and substitution of bpy for two molecules of isocyanide took place. When the (2-R-aryl)palladium(II) complex (R = C(O)Me, CN, CH═CH_2) contained PPh_3 as the only neutral ligand, reactions with XyNC in a 1:3 molar ratio led to monoinserted products in which PPh_3 had been substituted by XyNC, but only when reactions were carried out in CH_2Cl_2 under nitrogen and were stopped almost immediately after mixing the reactants. When these reactions were carried out with a long reaction time and in a 1:4 molar ratio, triinserted complexes were isolated. The reaction of (2-R-aryl)palladium(II) complexes when R = CHO with XyNC usually led to complex mixtures. Only in one case (reaction of **1c** with XyNC in a 1:5 molar ratio) were we able to isolate a complex resulting from the triinsertion of XyNC followed by a nucleophilic attack at the formyl carbon of the nitrogen of the primarily inserted isocyanide. Metathesis reactions of some bromo complexes with Tl(TfO) gave triflato complexes, a cyclopalladated aquo complex, or an unusual trinuclear complex in which a dimeric (2-cyanoaryl)palladium complex acts as a chelating ligand of the Pd(C_6H_4CN-2)PPh_3 moiety. The structure and stability of some complexes provide new data on the concept of transphobia. The extensive structural data allow the proposal of various scales of trans influence and a connection of these with the scale of transphobia.

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Supporting Information Available: Listings of all refined and calculated atomic coordinates, all anisotropic thermal parameters, and all bond lengths and angles for the complexes **5b**, **6b**, **7d**, **8a**·$^1/_2CH_2Cl_2$, **8b**·$^1/_2CH_2Cl_2$, **9**, **10**·CH_2Cl_2, **11a**·$^1/_2CHCl_3$, **11b**, **12a**, and **13b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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