Synthesis of Palladium Complexes with *ortho*-Functionalized Aryl Ligands

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The complexes [Pd(C_6H_4X-2)BrL_2] (L_2 = *trans*-$(PR_3)_2$, R = Ph, X = CH=CH_2 (**1a**), CHO (**1b**), C(O)Me (**1c**), CN (**1d**); R = *p*-To = 4-tolyl, X = CH=CH_2 (**1a′**); L_2 = bpy = 2,2′-bipyridine, X = CHO (**2b**), C(O)Me (**2c**), CN (**2d**); L_2 = tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, X = CHO (**2b′**), CN (**2d′**)) have been prepared by oxidative addition of the corresponding bromoarene BrC_6H_4X-2 to "Pd(dba)$_2$" (=[Pd_2(dba)$_3$]·dba, dba = dibenzylideneacetone) in the presence of the appropriate ligand. The compound [Pd{C_6H_4(CH=CH_2)-2}(bpy)(PPh_3)]TfO (**3a**; TfO = CF_3SO_3) has been obtained by reacting **1a** with bpy in the presence of TlOTf. The cyclopalladated [Pd{κ^2-*C*,*O*-C_6H_4{C(O)Me}-2}(bpy)]TfO (**4c**) has been prepared from **2c** and TlOTf. The dimeric complexes [Pd(μ-Br)(C_6H_4X-2)$(PR_3)]_2$ (R = Ph, X = CHO (**5b**), C(O)-Me (**5c**), CN (**5d**); R = *o*-To = 2-tolyl, X = CHO (**5b″**), CN (**5d″**)) have been synthesized by reacting complexes **1b**−**d** with [$PdCl_2$($NCPh)_2$] in a 2:1 molar ratio or C_6H_4Br-1-X-2 with "Pd(dba)$_2$" and P(*o*-To)$_3$ in 1:1:1 molar ratio. The latter method leads to the monomeric [Pd{κ^2-*C*,*O*-C_6H_4{C(O)Me}-2}]Br{P(*o*-To)$_3$}] (**6c″**) when X = C(O)Me. The complex **2c** reacts with the alkyne PhC≡CPh or EtC≡CEt and TlOTf to give 1-methyl-2,3-diphenyl-1*H*-indenol (**7**) or 1-methyl-2,3-diethyl-1*H*-indenol (**8**), respectively. The crystal structures of complexes **1a**·2CH_2Cl_2, **1b**·CH_2Cl_2, **2b**,**d**, and **6c″** have been determined by X-ray diffraction studies. An interesting supramolecular layered structure is formed through CN···H−C_{bpy} and Br···H−C_{bpy} hydrogen bonds in complex **2d**.

Introduction

Arylpalladium chemistry constitutes a subject of current interest because of the involvement of such compounds in many palladium-catalyzed organic reactions.[1−3] We are interested in the synthesis and structure of palladium complexes with functionalized aryl ligands in order to study their reactivity with alkynes,[4−12] isocyanides,[12,13] CO[13,14] and other unsaturated reagents.[15] Thus, we have prepared complexes containing aryl groups such as $C_6H(OMe)_3$-3,4,5-CHO-2, $C_6H(OMe)_3$-2,3,4-X-6 (X = CHO, C(O)Me, CH_2OEt, C(O)NHBu^t),[12,16−18] and $C_6H_3(CHO)_2$-2,5.[19] Some of these complexes show interesting supramolecular structures with hydrogen bonds involving the functional

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groups incorporated in the aryl group, and we report in this paper an interesting layer structure formed in such a manner. We have also studied the reactivity of these aryl complexes with alkynes, obtaining different products depending on the aryl substituents, the other ligands coordinated to the palladium atom, and the reaction conditions. In some cases we have obtained highly functionalized indenylpalladium derivatives,[11] but in other cases depalladation occurs, giving organic compounds such as indenones and indenols,[10] benzofulvenes, or spirocyclic compounds.[5,6,9,10,12] These stoichiometric reactions could help to elucidate the mechanism of some palladium-catalyzed reactions involving the same haloarenes. Thus, indenones and indenols have been prepared by reacting 2-halobenzaldehyde and 2-haloaryl ketones with alkynes using Pd(0) as catalyst[20−23] and 3-oxo-1,3-dihydro-1-isobenzofuranyl alkanoates have been prepared by reacting 2-bromobenzaldehyde with sodium alkanoates under carbon monoxide pressure in the presence of a catalytic amount of $[PdCl_2(PPh_3)_2]$.[24]

The above-mentioned palladium complexes were prepared using the corresponding arylmercurials as transmetalating agents, since they are compatible with the reactive substituents present in the aryl groups. In this paper, we describe the synthesis of (*o*-X-phenyl)palladium complexes with X = CHO, C(O)Me, CH=CH_2, and CN through oxidative addition reactions. We have used this method for the preparation of *o*-aminoaryl derivatives.[14,25] To the best of our knowledge, the only (*o*-CHO-aryl)- or (*o*-C(O)Me-aryl)palladium complexes are our trimethoxy derivatives and a series of (2,5-diformylphenyl)palladium complexes;[16,17,19] furthermore, very few (*o*-alkenylaryl)palladium compounds are known,[26] among which are those prepared by us from (2,3,4-trimethoxy-6-formylphenyl)palladium derivatives and phosphorus ylides.[18] 2-Iodoalkenyl arenes have been reacted with diphenylacetylene, norbornene, or methylenecyclopropane to give various organic compounds using Pd(0) as catalyst.[27] The compound [Pd{C_6H_4CN-2}Cl(PPh_3)$_2$} appeared in a patent.[28] Recently, the catalytic synthesis of 2,3-diphenylindenone has been reported, resulting from the reaction of 2-iodobenzonitrile with diphenylacetylene using $Pd(dba)_2$ as catalyst.[29]

Experimental Section

The IR and NMR spectra, elemental analyses, conductivity measurements in acetone and melting-point determinations were carried out as described earlier.[30] Long-range CH correlations of **2b**, **2b′**, **2c**, **2d**, and **2d′** were determined on a Bruker DPX 300 apparatus. The compounds "Pd(dba)$_2$" ([Pd_2(dba)$_3$]·dba, dba = dibenzylideneacetone)[1,31] and [$PdCl_2$(NCPh)$_2$][32] were prepared as reported previously. The 2-haloarenes were purchased from Fluka. In the complexes containing the ligand 2,2′-bipyridine, the atoms marked with a prime correspond to the ring trans to the aryl group.

Synthesis of *trans*-[Pd{C_6H_4(CH=CH_2)-2}Br(PPh_3)$_2$] (1a). "Pd(dba)$_2$" (150 mg, 0.26 mmol), PPh_3 (137 mg, 0.52 mmol), and 2-bromostyrene (51 μL, 0.39 mmol) were mixed under nitrogen in toluene (15 mL). The mixture was heated quickly to boiling and refluxed for 10 min. The color changed from red to yellow. The solvent was removed under vacuum, the residue extracted with dichloromethane, and the extracts filtered over anhydrous $MgSO_4$. From this point the workup was carried out in the air. The resultant yellow solution was evaporated under vacuum to dryness and diethyl ether added, precipitating a yellow solid which was filtered, washed with diethyl ether, and dried to give **1a**. Yield: 158 mg, 75%. Mp: 115 °C dec. Anal. Calcd for $C_{44}H_{37}BrP_2Pd$: C, 64.92; H, 4.58. Found: C, 64.93; H, 4.50. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.8−7.15 (several m, 30H, PPh_3), 6.97 (dd, 1H, C*H*=CH_2, $^3J_{HH}$ = 17 Hz, $^3J_{HH}$ = 11 Hz), 6.91−6.86 (m, 1H, C_6H_4), 6.47−6.42 (m, 2H, C_6H_4), 6.28−6.23 (m, 1H, C_6H_4), 5.20 (dd, 1H, CH=CH_2 *trans* to H, $^2J_{HH}$ = 1 Hz, $^3J_{HH}$ = 17 Hz), 4.84 (dd, 1H, CH=CH_2 *cis* to H, $^2J_{HH}$ = 1 Hz, $^3J_{HH}$ = 11 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 158.28 (t, C−Pd C_6H_4, $^2J_{PC}$ = 3 Hz), 142.04 (t, *C*-CH=CH_2, $^3J_{PC}$ = 3 Hz), 141.08 (t, *C*H=CH_2, $^4J_{PC}$ = 2 Hz), 135.63 (t, C6 C_6H_4, $^3J_{PC}$ = 5 Hz), 134,70 (t, *ortho* C's PPh_3, J_{PC} = 6 Hz), 131,27 (t, *ipso* C's PPh_3, J_{PC} = 23 Hz), 129.66 (s, *para* C's PPh_3), 127.69 (t, *meta* C's PPh_3, J_{PC} = 5 Hz), 126.71 (s, CH C_6H_4), 126.06 (s, CH C_6H_4), 122.67 (s, CH C_6H_4), 111.64 (s, CH_2). ^{31}P NMR (121 MHz, $CDCl_3$): δ 22.87 (s).

Synthesis of *trans*-[Pd{C_6H_4(CH=CH_2)-2}Br{P(*p*-To)$_3$}$_2$] (1a′). Complex **1a′** was similarly prepared from "Pd(dba)$_2$" (150 mg, 0.26 mmol), P(*p*-To)$_3$ (*p*-To = 4-tolyl; 159 mg, 0.52 mmol), and 2-bromostyrene (51 μL, 0.39 mmol). Color: pale brown. Yield: 160 mg, 68%. Mp: 138 °C dec. Anal. Calcd for $C_{50}H_{49}BrP_2Pd$: C, 66.86; H, 5.50. Found: C, 66.70; H, 5.46. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.8−6.8 (several m, 26H), 6.41 (m, 2H, C_6H_4, J = 4 Hz), 6.22 (m, C_6H_4, 1H), 5.20 (dd, 1H, CH=CH_2, H trans to H, $^2J_{HH}$ = 1 Hz, $^3J_{HH}$ = 17 Hz), 4.81 (dd, 1H, CH=CH_2, H *cis* to H, $^2J_{HH}$ = 1 Hz, $^3J_{HH}$ = 11 Hz), 2.30 (s, 18H, Me). ^{13}C NMR (50 MHz, $CDCl_3$): δ 158,87 (t, C−Pd, $^2J_{PC}$ = 3 Hz), 142.00 (t, *C*-CH=CH_2, $^3J_{PC}$ = 3 Hz), 141.42 (t, *C*H=CH_2, $^4J_{PC}$ = 2 Hz), 139.48 (s, *para* C's P(*p*-To)$_3$), 135.60 (t, C6 C_6H_4, $^3J_{PC}$ = 5 Hz), 134.60 (t, *ortho* C's P(*p*-To)$_3$, J_{PC} = 6 Hz), 128.39 (t, *meta* C's P(*p*-To)$_3$, J_{PC} = 5 Hz), 128.36 (t, *ipso* C's P(*p*-To)$_3$, J_{PC} = 24 Hz), 126.48 (s, CH C_6H_4), 125.84 (s, CH C_6H_4), 122.17 (s, CH C_6H_4), 119.29 (s, CH_2), 21.36 (s, Me). ^{31}P NMR (121 MHz, $CDCl_3$): δ 21.01 (s).

Synthesis of *trans*-[Pd{C_6H_4(CHO)-2}Br(PPh_3)$_2$] (1b). Complex **1b** was similarly prepared from "Pd(dba)$_2$" (150 mg, 0.26 mmol), PPh_3 (137 mg, 0.52 mmol), and 2-bromobenzaldehyde (45 μL, 0.39 mmol). Color: pale yellow. Yield: 168 mg, 79%. Mp: 184 °C dec. Anal. Calcd for $C_{43}H_{35}BrOP_2Pd$: C, 63.29; H, 4.32. Found: C, 63.22; H, 4.36. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.69 (s, 1H, CHO), 7.55−6.58 (several m, 34 H, PPh_3 and C_6H_4). ^{13}C NMR (50 MHz, $CDCl_3$): δ 194.54 (s, CHO), 168.52 (t, C−Pd, $^2J_{PC}$ = 4 Hz), 140.07 (s, *C*-CHO), 135.14 (t, C6 C_6H_4, $^3J_{PC}$ = 4 Hz), 134.51 (t, *ortho* C's PPh_3, J_{PC} = 6 Hz), 133.04 (s, CH C_6H_4), 131.09 (s, CH C_6H_4), 130.71 (t, *ipso* C's PPh_3, J_{PC} = 23 Hz), 129.83 (s, *para* C's PPh_3), 127.86 (t, *meta* C's PPh_3, J_{PC} = 5 Hz), 122.51 (s, C4 C_6H_4). ^{31}P NMR (121 MHz,

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$CDCl_3$): δ 23.17 (s). IR (cm^{-1}): ν(CO) 1682 (solid) 1684 (dichloromethane solution).

Synthesis of *trans*-[Pd{C_6H_4{C(O)Me}-2}Br(PPh_3)$_2$] (1c). "Pd(dba)$_2$" (200 mg, 0.35 mmol), PPh_3 (184 mg, 0.70 mmol), and 2-bromoacetophenone (71 μL, 0.52 mmol) were mixed in toluene (20 mL), under nitrogen. The mixture is slowly heated and kept at the boiling point for 10 min. The workup was continued in the air. The residue was extracted with dichloromethane (4 × 10 mL), and the combined extracts were filtered over anhydrous $MgSO_4$. The resultant solution was evaporated and diethyl ether added, precipitating a solid which was filtered, washed with diethyl ether, and dried to give **1c** as a yellow solid. Yield: 209 mg, 72%. Mp: 285 °C dec. Anal. Calcd for $C_{44}H_{37}BrOP_2Pd$: C, 63.67; H, 4.49. Found: C, 63.40; H, 4.80. ^{1}H NMR (300 MHz, $CDCl_3$; −60 °C): δ 7.60−7.17 (several m, 31H), 6.76 (d, 1H, C_6H_4, $^3J_{HH}$ = 7 Hz), 6.65 (t, 1H, C_6H_4, $^3J_{HH}$ = 7 Hz), 6.57 (t, 1H, C_6H_4, $^3J_{HH}$ = 7 Hz), 1.76 (s, 3H, Me). ^{13}C NMR (50 MHz, $CDCl_3$): δ 198.40 (s, CO), 165.68 (s, C−Pd), 141.04 (s, *C*C(O)Me), 135.32 (bs, C6 C_6H_4), 134.67 (t, *ortho* C's PPh_3, J_{PC} = 5 Hz), 133.24 (s, CH C_6H_4), 131,26 (t, *ipso* C's PPh_3, J_{PC} = 22 Hz), 129.50 (s, *para* C's PPh_3), 127.68 (bs, *meta* C's PPh_3), 121.83 (s, CH C_6H_4), 26.76 (s, Me). ^{31}P NMR (121 MHz, $CDCl_3$): δ, 23.05 (s). IR (cm^{-1}): ν(CO) 1660 (Nujol).

Synthesis of *trans*-[Pd{C_6H_4(CN)-2}Br(PPh_3)$_2$] (1d). Complex **1d** was prepared as described for **1a** from "Pd(dba)$_2$" (150 mg, 0.26 mmol), PPh_3 (137 mg, 0.52 mmol), and 2-bromobenzonitrile (71 mg, 0.39 mmol). Color: white. Yield: 163 mg, 76%. Mp: 215 dec. Anal. Calcd for $C_{43}H_{34}NP_2Pd$: C, 63.53; H, 4.22; N, 1.72. Found: C, 63.28; H, 4.36; N, 1.64. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.7−7.1 (several m, 31 H), 6.61−6.55 (m, 1H), 6.41−6.39 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.14 (t, C−Pd, $^2J_{PC}$ = 5 Hz), 135.67 (t, C6 C_6H_4, $^3J_{PC}$ = 4 Hz), 134,68 (t, *ortho* C's PPh_3, J_{PC} = 6 Hz), 132.84 (s, CH C_6H_4), 130.61 (t *ipso* C's PPh_3, J_{PC} = 23 Hz), 129.94 (s, *para* C's PPh_3), 129.71 (s, CH C_6H_4), 127.91 (t, *meta* C's PPh_3, J_{PC} = 5 Hz), 122.20 (s, C4 C_6H_4), 121.79 (s, CN), 120.29 (t, *C*-CN, $^3J_{PC}$ = 4 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 23.32 (s). IR (cm^{-1}): ν(CN) 2212 (Nujol).

Synthesis of [Pd{C_6H_4(CHO)-2}Br(bpy)] (2b). "Pd(dba)$_2$" (150 mg, 0.26 mmol), bpy (2,2′-bipyridine; 41 mg, 0.26 mmol), and 2-bromobenzaldehyde (45 μL, 0.39 mmol) were mixed in toluene (15 mL) under nitrogen. The red mixture was slowly heated over 1 h 20 min until the color changed to orange-yellow (at ca. 90 °C) and then evaporated to dryness. Workup as for **1c** rendered **2b** as a yellow solid. Yield: 93 mg, 80%. Mp: 190 °C dec. Anal. Calcd for $C_{17}H_{13}BrN_2OPd$: C, 45.62; H, 2.93; N, 6.26. Found: C, 45.74; H, 2.84; N, 6.10. ^{1}H NMR (200 MHz, $CDCl_3$): δ 11.09 (s, 1H, CHO), 9.42 (d, 1H, H6′ bpy, $^3J_{HH}$ = 5 Hz), 8.14−8.05 (several m, 3H, H3, H3′ and H4′ bpy), 8.00 (td, 1H, H4 bpy, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.78 (dd, 2H, aryl H3 and H6, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.64−7.57 (m, 1H, H5′ bpy), 7.52 (dd, 1H, H6 bpy, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz), 7.31−7.21 (m, 2H, aryl H5 and H5 bpy), 7.09 (t, 1H, aryl H4, $^3J_{HH}$ = 7 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 196.73 (s, CHO), 159.50 (s, C−Pd), 156.12 (s, C2 bpy), 153.44 (s, C2′ bpy), 150.67 (s, C6 or 6′ bpy), 150.59 (s, C6′ or 6 bpy), 141.39 (s, *C*−CHO), 139.24 (s, C4′ bpy), 139.06 (s, C4 bpy), 136.46 (s, C6 C_6H_4), 131.97 (s, C5 C_6H_4), 128.30 (s, C3 C_6H_4), 126.81 (b s, C5 and 5′ bpy), 124.02 (s, C4 C_6H_4), 122.40 (s, C3 bpy), 121.67 (s, C3′ bpy). IR (cm^{-1}): ν(CO) 1682 (Nujol).

Synthesis of [Pd{C_6H_4(CHO)-2}Br(tmeda)] (2b′): as described for **2b**, from "Pd(dba)$_2$" (150 mg, 0.26 mmol), tmeda (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine; 39 μL, 0.26 mmol), and 2-bromobenzaldehyde (45 μL, 0.39 mmol). Color: yellow. Yield: 76 mg, 72%. Mp: 181 °C dec. Anal. Calcd for $C_{13}H_{21}BrN_2OPd$: C, 38.31; H, 5.19; N, 6.87. Found: C, 38.51; H, 5.23; N, 6.89. ^{1}H NMR (200 MHz, $CDCl_3$): δ 11.07 (s, 1H, CHO), 7.66 (dd, 1H, H3, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 7.61 (dd, 1H, H6, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.16 (td, 1H, H5, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 7.00 (b t, 1H, H4, $^3J_{HH}$ = 7 Hz), 3.0−2.3 (m, 4H, 2 × CH_2), 2.73 (s, 3H, Me), 2.70 (s, 3H, Me), 2.53 (s, 3H, Me), 2.17 (s, 3H, Me). ^{13}C NMR (50 MHz, $CDCl_3$): δ 196.99 (s, CHO), 158.98 (s, C−Pd), 141.67 (s, *C*−CHO), 136.08 (s, C6), 131.26 (s, C5), 128.89 (s, C3), 123.46 (s, C4), 62.72 (s, CH_2), 58.45 (s, CH_2), 51.74 (s, Me), 49.68 (s, Me), 49.27 (s, Me), 47.96 (s, Me). IR (cm^{-1}): ν(CO) 1682 (Nujol).

Synthesis of [Pd{C_6H_4C(O)Me}-2}Br(bpy)] (2c). "Pd(dba)$_2$" (300 mg, 0.52 mmol), bpy (81 mg, 0.52 mmol), and 2-bromoacetophenone (101 mg, 0.75 mmol) were mixed in toluene (20 mL), under nitrogen. The mixture was slowly heated until the color changed to brown (1 h 20 min, 90 °C). Workup as for **1c** rendered yellow **2c**. Yield: 180 mg, 75%. Mp: 210 °C. Anal. Calcd for $C_{18}H_{15}BrN_2OPd$: C, 46.83; H, 3.27; N, 6.07. Found: C, 46.68; H, 3.17; N, 5.90. ^{1}H NMR (300 MHz, $CDCl_3$; −60 °C): δ 9.45 (d, 1H, bpy, $^3J_{HH}$ = 5 Hz), 8.14 (m, 3H), 8.05 (t, 1H, $^3J_{HH}$ = 8 Hz), 7.83 (t, 2H, J_{HH} = 8 Hz), 7.63 (t, 1H, J_{HH} = 6 Hz), 7.57 (d, 1H, J_{HH} = 6 Hz), 7.35−7.23 (m, 2H), 7.13 (t, 1H, J_{HH} = 7 Hz), 2.86 (s, 3H, Me). ^{13}C NMR (50 MHz, $CDCl_3$): δ 203.17 (s, CO), 152.70 (s, C−Pd), 150.95 (bs, C6 and 6′ bpy), 144.44 (*C*−C(O)Me), 138.66 (bs, C4 and 4′ bpy), 136.94 (s, C6 C_6H_4), 129.96 (s, C5 C_6H_4), 129.71 (s, C3 C_6H_4), 126.57 (b s, C5 and 5′ bpy), 123.30 (s, C4 C_6H_4), 121.70 (b s, C3 and 3′ bpy), 30.30 (s, Me). IR (cm^{-1}): ν(CO) 1660 (Nujol).

Synthesis of [Pd{C_6H_4(CN)-2}Br(bpy)] (2d). "Pd(dba)$_2$" (150 mg, 0.26 mmol), bpy (41 mg, 0.26 mmol), and 2-bromobenzonitrile (71 mg, 0.39 mmol) were mixed in toluene (15 mL) under nitrogen. The red mixture was heated for 30 min, until the temperature reached 100 °C. The color changed to greenish brown. Workup was then continued in air. The solvent was removed under vacuum and the residue extracted with dichloromethane (2 × 10 mL). The combined extracts were filtered over anhydrous $MgSO_4$, the resulting solution was evaporated to dryness, and the residue was triturated with diethyl ether, giving a yellow solid of **2d** which was filtered, washed with diethyl ether, and dried. Yield: 66 mg, 56%. Mp: 175 °C dec. Anal. Calcd for $C_{17}H_{12}BrN_3Pd$: C, 45.93; H, 2.72; N, 9.45. Found: C, 45.80; H, 2.45; N, 9.11. ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.16 (d, 1H, H6′ bpy, $^3J_{HH}$ = 5 Hz), 8.69−8.63 (m, 2H, H3 and H3′ bpy), 8.30 (dt, 2H, H4 and 4′ bpy, J_{HH} = 7 Hz, J_{HH} = 1 Hz), 7.84 (t, 1H, H5′ bpy, J_{HH} = 6 Hz), 7.65 (t, 1H, H5 bpy, J_{HH} = 6 Hz), 7.55−7.51 (m, aryl H3, aryl H6, and H6 bpy, 3H), 7.28 (dt, 1H, aryl H5, J_{HH} = 7 Hz, J_{HH} = 1 Hz), 7.10 (t, 1H, aryl H4, J_{HH} = 7 Hz). ^{13}C NMR (50 MHz, d_6-dimethyl sulfoxide): δ 156.24 (s, C1 C_6H_4), 155.83 (s, C2 bpy), 153.66 (s, C2′ bpy), 149.69 (s, C6 bpy), 149.43 (s, C6′ bpy), 140.40 (s, 2C, C4 and 4′ bpy), 137.34 (s, C6 C_6H_4), 132.38 (s, C3 C_6H_4), 130.21 (s, C5 C_6H_4), 127.70 (s, C5 bpy), 127.37 (s, C5′ bpy), 123.98 (s, C3 bpy), 123.89 (s, C4 C_6H_4), 123.25 (s, C3′ bpy), 121.41 (s, CN), 118.88 (s, *C*−CN). IR (cm^{-1}): ν(CN) 2218 (Nujol).

Synthesis of [Pd{C_6H_4(CN)-2}Br(tmeda)] (2d′). Complex **2d′** was similarly prepared from "Pd(dba)$_2$" (150 mg, 0.26 mmol), tmeda (39 μL, 0.26 mmol), and 2-bromobenzonitrile (71 mg, 0.39 mmol), but the mixture was slowly heated to boiling and kept at the boiling point for a further 10 min. Color: pale brown. Yield: 67 mg, 63%. Mp: 141 °C dec. Anal. Calcd for $C_{13}H_{20}BrN_3Pd$: C, 38.59; H, 4.98; N, 10.38. Found: C, 38.67; H, 4.84; N, 9.91. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.40 (dd, 1H, H6, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.34 (dd, 1H, H3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.13 (td, 1H, H5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 6.91 (td, 1H, H4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 3.0−2.3 (m, 4H, 2 × CH_2), 2,74 (s, 3H, Me), 2.66 (s, 3H, Me), 2.56 (s, 3H, Me), 2.46 (s, 3H, Me). ^{13}C NMR (50 MHz, d_6-$CDCl_3$): δ 156.05 (s, CPd), 136.27 (s, C6), 131.63 (s, C3), 129.66 (s, C5), 123.00 (s, C4), 122.03 (s, CN), 119.62 (s, *C*CN), 62.45 (s, CH_2), 58.34 (s, CH_2), 51.13 (s, Me), 49.78 (s, Me), 48.87 (s, Me), 47.94 (s, Me). IR (cm^{-1}): ν(CN) 2214 (Nujol).

Synthesis of [Pd{C_6H_4(CH=CH_2)-2}(bpy)(PPh_3)]TfO (3a). TlOTf (TfO = CF_3SO_3; 65 mg, 0.18 mmol) and bpy (29 mg, 0.18 mmol) were added to a solution of **1a** (150 mg, 0.18 mmol) in dichloromethane (15 mL), and the mixture was

stirred at room temperature overnight. The suspension was filtered over Celite, the solution evaporated to dryness, and the residue triturated with diethyl ether to give **3a** as a yellow solid. Yield: 124 mg, 88%. Mp: 156 °C dec. Λ_M (acetone): 116 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{37}H_{30}F_3N_2O_3PdS$: C, 57.19; H, 3.89; N, 3.60; S, 4.13. Found: C, 57.25; H, 3.81; N, 3.46; S, 3.89. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.79 (d, 1H, bpy, $^3J_{HH}$ = 8 Hz), 8.24−8.14 (m, 1H), 7.72−6.72 (several m, 26H), 5.46 (dd, 1H, CH=CH_2 H *trans* to H, $^3J_{HH}$ = 18 Hz, $^2J_{HH}$ = 1 Hz), 5.04 (dd, 1H, CH=CH_2 H *cis* to H, $^3J_{HH}$ = 11 Hz, $^2J_{HH}$ = 1 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 32.61 (s).

Synthesis of [Pd{κ^2-*C,O*-C$_6$H$_4$\{C(O)Me\}-2}(bpy)]TfO (4c). TlOTf (46 mg, 0.13 mmol) was added to **1c** (60 mg, 0.13 mmol) in acetone (17 mL), and the mixture was stirred for 1 h. The suspension was filtered over Celite and the resulting solution evaporated to dryness. Addition of diethyl ether causes the precipitation of a solid, which was filtered, washed with diethyl ether, and dried to give **4c** as a yellow solid. Yield: 60 mg, 87%. Mp: 172 °C dec. Λ_M (acetone): 150 Ω^{-1} cm^2 mol^{-1}. NMR: not sufficiently soluble. Anal. Calcd for $C_{19}H_{15}F_3N_2O_3PdS$: C, 42.99; H, 2.85; N, 5,28; S, 6.04. Found: C, 42.68; H, 2.95; N, 5.29; S, 5.82. IR (cm^{-1}): ν(C=O) 1582 (Nujol).

Synthesis of [Pd$_2$(μ-Br)$_2$\{C$_6$H$_4$(CHO)-2\}$_2$(PPh$_3$)$_2$] (5b). [$PdCl_2$(NCPh)$_2$] (48 mg, 0.13 mmol) was added to a dichloromethane solution (5 mL) of **1b** (200 mg, 0.25 mmol). The resulting yellow suspension was stirred for 30 min. Then, a large excess of NaBr (1.03 g, 10 mmol) was added and the mixture stirred for a further 10 min. The final suspension was filtered over Celite, the solid was washed with dichloromethane (3 × 5 mL), and the combined mother liquors were concentrated nearly to dryness. Diethyl ether (15 mL) was then added, precipitating a solid, which was filtered, washed with diethyl ether, and dried in air to give **5b** as a yellow solid. Yield: 132 mg, 95%. Mp: 212 °C dec. NMR: not sufficiently soluble. Anal. Calcd for $C_{50}H_{40}Br_2O_2P_2Pd_2$: C, 54.23; H, 3.64. Found: C, 53.90; H, 3.34. IR (cm^{-1}): ν(C=O) 1692 (Nujol).

Synthesis of [Pd$_2$(μ-Br)$_2$\{C$_6$H$_4$(CHO)-2\}$_2$\{P(*o*-To)$_3$\}$_2$] (5b″). "Pd(dba)$_2$" (150 mg, 0.26 mmol) and P(*o*-To)$_3$ (79 mg, 0.26 mmol) were mixed in toluene (20 mL) under nitrogen. After 10 min, 2-bromobenzaldehyde (45 μL, 0.39 mmol) was added and the mixture slowly heated until the red color disappeared (45 min, 80 °C). The solvent was evaporated under vacuum, the resulting residue was extracted with dichloromethane (4 × 10 mL), and the combined extracts were filtered over anhydrous $MgSO_4$. The resultant yellow solution was evaporated to dryness and diethyl ether added, precipitating a solid which was filtered, washed with diethyl ether, and air-dried to give **5b″** as a yellow solid. Yield: 82 mg, 53%. Mp: 210 °C dec. Anal. Calcd for $(C_{28}H_{26}BrOPPd)_2$: C, 56.45; H, 4.40. Found: C, 56.54; H, 4.14. ^{1}H NMR (300 MHz, $CDCl_3$, −60 °C): δ 11.60 (bs, 1H, CHO), 9.59 (dd, 1H, H6 *o*-To *endo*, $^3J_{PH}$ = 19 Hz, $^3J_{HH}$ = 7 Hz), 7.9−6.5 (several m, 15H), 3.61 (s, 3H, Me), 1.46 (s, 3H, Me), 0.91 (s, 3H, Me). ^{31}P NMR (121 MHz, $CDCl_3$, −60 °C): δ 27.83 (s). IR (cm^{-1}): ν(C=O) 1682 (Nujol).

Synthesis of [Pd$_2$ (μ-Br)$_2$\{C$_6$H$_4$\{C(O)Me\}-2\}$_2$(PPh$_3$)$_2$] (5c). Complex **5c** was prepared as described for **5b** from **1c** (350 mg, 0.42 mmol) and [$PdCl_2$(NCPh)$_2$] (81 mg, 0.21 mmol). Since the elemental analyses were unsatisfactory, the resulting solid was applied to a preparative TLC and eluted with hexane/dichloromethane (1:3). The immobile fraction was collected to give pure **5c** as a yellow solid. Yield: 174 mg, 73%. Mp: 195 °C dec. Anal. Calcd for $C_{52}H_{44}Br_2O_2P_2Pd_2$: C, 55.01; H, 3.91. Found: C, 54.83; H, 3.96. ^{1}H NMR (300 MHz, $CDCl_3$, −60 °C): δ 7.8−7.2 (several m, 16H), 7.08 (t, 1H, C_6H_4, J_{HH} = 7 Hz), 6.83 (t, 1H, C_6H_4, J_{HH} = 7 Hz), 6.38 (t, 1H, C_6H_4, J_{HH} = 7 Hz), 2.81 (s, 3H, Me). ^{31}P NMR (121 MHz, $CDCl_3$, −60 °C): δ 49.64 (s). IR (cm^{-1}): ν(C=O) 1660 (Nujol).

Synthesis of [Pd$_2$(μ-Br)$_2$\{C$_6$H$_4$(CN)-2\}$_2$(PPh$_3$)$_2$] (5d). Complex **5d** was prepared by following the procedure described for **5b** from **1d** (200 mg, 0.25 mmol) and [$PdCl_2$(NCPh)$_2$] (47 mg, 0.12 mmol). Color: yellow. Yield: 118 mg, 87%. Mp: 228 °C dec. NMR: not sufficiently soluble. Anal. Calcd for $(C_{25}H_{19}BrOPPd)_2$: C, 54.53; H, 3.48; N, 2.54. Found: C, 54.17; H, 3.34; N, 2.55. IR (cm^{-1}): ν(CN) 2220 (Nujol).

Synthesis of [Pd$_2$(μ-Br)$_2$\{C$_6$H$_4$(CN)-2\}$_2$\{P(*o*-To)$_3$\}$_2$] (5d″). "[Pd(dba)$_2$]" (200 mg, 0.35 mmol) and P(*o*-To)$_3$ (107 mg, 0.35 mmol) were mixed in toluene (20 mL) under nitrogen. Then, 2-bromobenzonitrile (95 mg, 0.52 mmol) was added, and the resultant suspension was slowly heated until the red color disappeared (25 min, 80 °C). The solvent was evaporated under vacuum, the residue was extracted with dichloromethane (4 × 10 mL), the combined extracts were filtered over Celite, and the resulting solution was evaporated in vacuo. Addition of diethyl ether (15 mL) precipitated a solid which was filtered, washed with diethyl ether, and air-dried to give **5d″** as a yellow solid. Yield: 47 mg, 23%. Mp: 300 °C dec. NMR: not sufficiently soluble. Anal. Calcd for $(C_{28}H_{25}BrNPPd)_2$: C, 56.73; H, 4.25; N, 2.36. Found: C, 56.70; H, 4.55; N, 2.39. IR (cm^{-1}): ν(CN) 2214 (Nujol).

Synthesis of [Pd{κ^2-*C,O*-C$_6$H$_4$\{C(*O*)Me\}-2}Br\{P(*o*-To)$_3$\}] (6c″). "[Pd(dba)$_2$]" (200 mg, 0.35 mmol) and P(*o*-To)$_3$ (107 mg, 0.35 mmol) were mixed in toluene (20 mL) under nitrogen. Then, 2-bromoacetophenone (70 μL, 0.52 mmol) was added, and the resultant suspension was slowly heated until the red color disappeared (20 min, 70 °C). The solvent was evaporated under vacuum, the residue was extracted with dichloromethane (4 × 10 mL), the combined extracts were filtered over Celite, and the resulting solution evaporated under vacuum. Addition of diethyl ether (15 mL) precipitated a solid which was filtered, washed with diethyl ether, and air-dried to give **6c″** as a yellow solid. Yield: 120 mg, 56%. Mp: 205 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.70 (dd, 1H, H6 *endo o*-To, $^3J_{PH}$ = 18 Hz, $^3J_{HH}$ = 8 Hz), 7.5−7.1 (several m, 11H), 6.98 (t, 1H, J_{HH} = 7 Hz), 6.76 (t, 1H, J_{HH} = 7 Hz), 6.49 (t, 1H, J_{HH} = 7 Hz), 3.27 (s, 3H, Me), 2.71 (s, 3H, COMe), 2.09 (s, 3H, Me), 1.68 (s, 3H, Me). ^{31}P NMR (121 MHz, $CDCl_3$): δ 38.37 (s). Anal. Calcd for $C_{29}H_{28}BrOPPd$: C, 57.12; H, 4.63. Found: C, 57.14; H, 4.69. IR (cm^{-1}): ν(C=O) 1586 (Nujol).

Synthesis of Indenols 7 and 8. PhC≡CPh (157 mg, 0.88 mmol) or EtC≡CEt (0.1 cm^3, 0.88 mmol) and TlOTf (156 mg, 0.44 mmol) were added to a solution of **2c** (200 mg, 0.44 mmol) in 15 cm^3 of CH_2Cl_2. The resulting suspension was stirred for 16 h at room temperature and then filtered over Celite. The red solution obtained was concentrated and chromatographed over silica gel containing a small amount of silica gel 60 GF254, using 1:2 hexane/CH_2Cl_2 as eluant. The first, colorless band was taken. The product was extracted with acetone, stirred with anhydrous $MgSO_4$, and filtered. Evaporation of the acetone gave **7** or **8** as a white solid. Yield: 92 mg, 70% (**7**); 60 mg, 67% (**8**). The NMR data of these indenols coincide with those reported in the literature.[33]

X-ray Structure Determinations. Compounds 1b·CH_2Cl_2 and 6c″. Data Collection and Reduction. Crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of the diffractometer (Bruker SMART 1000 CCD with LT-3 low-temperature apparatus). Measurements were conducted using monochromated Mo Kα radiation (ω-scans). Absorption corrections were based on multiple scans (program SADABS).

Structure Refinement. Structures were refined anisotropically against F^2 (program SHELXL-97, G. M. Sheldrick, University of Göttingen). H atoms were included using a riding model or with rigid methyl groups. Special aspects: for **1b**·CH_2Cl_2 the dichloromethane molecule is disordered over an inversion center.

Compounds 1a·2CH_2Cl_2, 2b, and 2d. Data Collection and Reduction. Crystals were mounted on glass fibers and transferred to the diffractometer as summarized in Table 1. Cell constants were refined from ca. 60 reflections in the 2θ

(33) Liebeskind, L. S.; Gasdaska, J. R.; McCallum, J. S.; Tremont, S. J. *J. Org. Chem.* **1989**, *54*, 669.

Table 1. Crystal Data for 1a·2CH_2Cl_2, 1b·CH_2Cl_2, 2b, 2d, and 6c″

	1a·2CH_2Cl_2	**1b**·CH_2Cl_2	**2b**	**2d**	**6c″**
formula	$C_{46}H_{41}BrCl_4P_2Pd$	$C_{43.5}H_{36}BrClOP_2Pd$	$C_{17}H_{13}BrN_2OPd$	$C_{17}H_{12}BrN_3Pd$	$C_{29}H_{28}BrOPPd$
M_r	959.88	858.42	447.61	444.61	609.79
source	vapor diffusion hexane/CH_2Cl_2	liquid diffusion hexane/CH_2Cl_2	liquid diffusion hexane/CH_2Cl_2	liquid diffusion hexane/CH_2Cl_2	liquid diffusion hexane/CH_2Cl_2
cryst habit	colorless prism	colorless block	yellow prism	yellow lath	pale yellow tablet
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
a, Å	11.7835(14)	11.7883(10)	9.6853(9)	9.8692(12)	17.9750(14)
b, Å	28.951(2)	18.9947(16)	13.5645(13)	13.799(2)	12.9761(10)
c, Å	12.9176(14)	16.7519(16)	11.6714(12)	11.7476(14)	21.532(2)
β, deg	99.891(8)	102.731(3)	91.354(6)	91.574(10)	90
V, Å^3	4341.3	3658.8	1532.9	1599.3	5022.3
Z	4	4	4	4	8
radiation used	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
T, K	173(1)	143	173(1)	293(2)	143
monochromator	graphite	graphite	graphite	graphite	graphite
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$Pbca$
cryst size, mm	0.45 × 0.32 × 0.28	0.33 × 0.20 × 0.17	0.60 × 0.20 × 0.14	0.42 × 0.20 × 0.14	0.20 × 0.17 × 0.06
μ, mm^{-1}	1.70	1.79	3.82	3.66	2.41
abs cor	ψ scans	SADABS	ψ scans	ψ scans	SADABS
max transmissn, %	0.91	0.94	0.98	0.86	0.99
min transmissn, %	0.75	0.67	0.74	0.70	0.73
diffractometer	Siemens P4	Bruker SMART	Siemens P4	Siemens P4	Bruker SMART
scan method	ω	ω	ω	ω	ω
2θ range, deg	6−50	3.4−60	6−50	6−50	3.8−60
hkl limits	$-h, -k, \pm l$	$\pm h, \pm k, +l$	$\pm h, -k, -l$	$\pm h, -k, -l$	$\pm h, \pm k, +l$
no. of rflns measd	9239	25 949	2873	3910	39 959
no. of indep rflns	7642	10 584	2693	2758	7321
R_{int}	0.032	0.029	0.023	0.020	0.079
R1[a]	0.040	0.033	0.031	0.029	0.030
wR2[b]	0.069	0.086	0.062	0.055	0.053
max $\Delta\rho$, e Å^{-3}	0.53	1.46	0.51	0.33	0.52

[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.

range 10−25°. The structure of **2b** was solved by direct methods, and the others were solved by the heavy-atom method and subjected to anisotropic full-matrix least-squares refinement against F^2 (program SHELXL-93, G. M. Sheldrick, University of Göttingen). H atoms were included using a riding model. For **1a**·2CH_2Cl_2 the final $R(F)$ ($I > 2\sigma(I)$) was 0.0403, for 487 parameters and 426 restraints; maximum $\Delta/\sigma = 0.001$. For compound **2b** the final $R(F)$ ($I > 2\sigma(I)$) was 0.0310, for 199 parameters and 175 restraints; maximum $\Delta/\sigma = 0.001$. For compound **2d** the final $R(F)$ ($I > 2\sigma(I)$) was 0.0290, for 199 parameters and 175 restraints; maximum $\Delta/\sigma = 0.001$. Restraints were applied to local symmetry, and U components of neighboring light atoms. The programs use the neutral atom scattering factors, $\Delta f'$ and $\Delta f''$ values, and absorption coefficients from ref 34.

Results and Discussion

Synthesis of Complexes. We have prepared the complexes **1**, **2**, **5b″**, **5d″**, and **6c″** by oxidative addition of the corresponding aryl bromides to [$Pd_2(dba)_3$]·dba ("Pd(dba)$_2$") in the presence of a stoichiometric amount of the ligand (Scheme 1). Such a procedure has been shown to be useful for the synthesis of organopalladium complexes containing nitrogen[35,36] or phosphorus donor ligands,[37] and we have recently applied it to the synthesis of palladated *o*-aniline derivatives.[14]

Brief refluxing in toluene (10 min) of a mixture of "Pd(dba)$_2$", PR_3, and 2-bromostyrene in an 1:2:1.5 molar ratio led to the complexes *trans*-[$Pd(C_6H_4X\text{-}2)Br(PR_3)_2$] (X = CH=$CH_2$, R = Ph (**1a**), *p*-To (=4-tolyl) (**1a′**)) (Scheme 1). Attempts to prepare **1a** under other reaction conditions (shorter reaction time or lower temperature) gave irresolvable mixtures. Complex **1a** can also be obtained by using [$Pd(PPh_3)_4$] instead of the mixture "Pd(dba)$_2$" + PR_3.

Similar reactions in the presence of nitrogen donor ligands such as 2,2′-bipyridine (bpy) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) lead to decomposition. A somewhat different behavior was observed with 2-bromobenzaldehyde, 2-bromoacetophenone, and 2-bromobenzonitrile. The reactions in the presence of PPh_3 were successful, yielding *trans*-[$Pd(C_6H_4X\text{-}2)Br(PR_3)_2$] (R = Ph, X = CHO (**1b**), C(O)Me (**1c**), CN (**1d**)), as were those using bpy or tmeda, giving the complexes *cis*-[$Pd(C_6H_4X\text{-}2)Br(L_2)$] ($L_2$ = bpy, X = CHO (**2b**), C(O)Me (**2c**), CN (**2d**); L_2 = tmeda, X = CHO (**2b′**), CN (**2d′**)). It was not possible to obtain the complex [$Pd(C_6H_4C(O)Me\text{-}2)Br(tmeda)$].

When complex **1a** is reacted with bpy in the presence of TlOTf, the cationic complex **3a** is formed. The cyclopalladated cation **4c** can be obtained from the reaction of **2c** with TlOTf. A similar reaction with **2b** gave a product that we could not characterize.

The complexes [$Pd(Ar)(\mu\text{-}X)]_2$ (X = Cl, AcO), obtained by cyclometalation of ArH, have been used in most alkyne,[7,10,13,38−50] in some isocyanide,[51−56] and in a few

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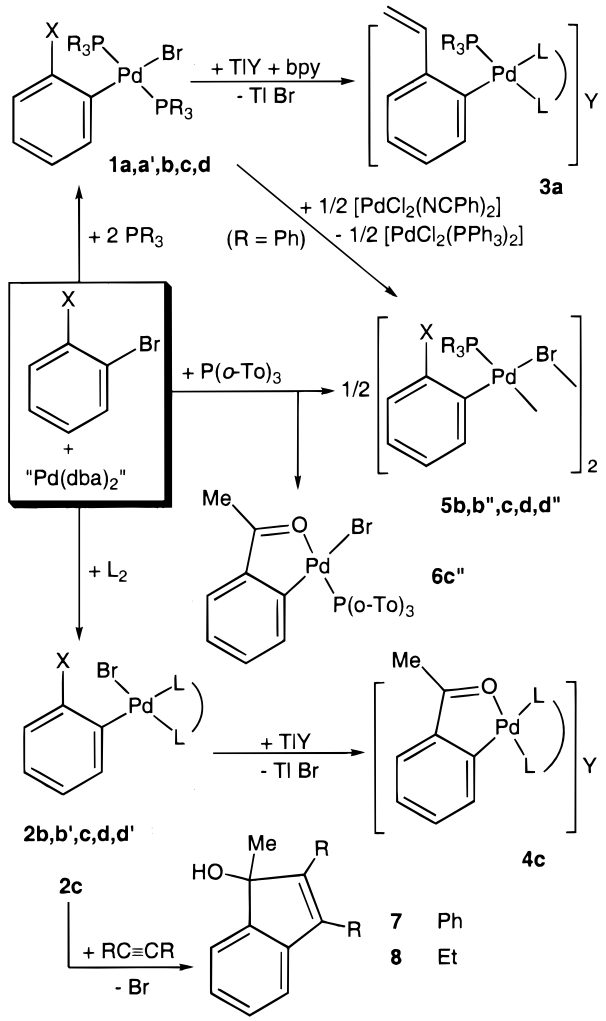
Scheme 1



R	X: CH=CH$_2$	CHO	C(O)Me	CN	L$_2$
Ph	**a**	**b**	**c**	**d**	bpy
p-To	**a'**	**b'**		**d'**	tmeda
o-To		**b"**	**c"**	**d"**	—

Y = TfO; To = C_6H_4Me

CO[51,52] insertion reactions. Therefore, for a future study of the reactivity of these arylpalladium complexes, we considered it of interest to synthesize the complexes [Pd(C_6H_4X-2)(μ-Br)(PR_3)]$_2$. The involvement of this type of complex in palladium-catalyzed C−N bond formation reactions has been shown.[3,57−60] We attempted the oxidative addition of the corresponding bromoarenes to a mixture of Pd(dba)$_2$ and PPh_3 in a 1:1 molar ratio but observed only the formation of the monomeric complexes **1b**−**d** in low yields. In the case of the reaction with 2-bromostyrene, the resonances due to the vinyl group were not present in the ^{1}H NMR spectrum of the product of the reaction. Nevertheless, it was possible to prepare the desired complexes [Pd(C_6H_4X-2)(μ-Br)(PPh_3)]$_2$ (X = CHO (**5b**), C(O)Me (**5c**), CN = (**5d**)) (Scheme 1) by reacting **1b**−**d** with [$PdCl_2$(NCPh)$_2$], following a procedure described for the synthesis of some $PhCH_2C$(O)[Pd] derivatives.[61] Again, the attempts to prepare **5a** through this method led to products without the vinyl group. This behavior is probably the result of the interchange between a phenyl group of PPh_3 and the aryl ligand, which is a very well-known process.[62−67] In contrast, the homologous complexes [Pd(C_6H_4X-2)(μ-Br){P(*o*-To)$_3$}]$_2$ (X = CHO (**5b″**), CN = (**5d″**)) were prepared by oxidative addition reactions of BrC_6H_4X-2 to [Pd(P(*o*-To)$_3$)$_2$][57,68,69] or to Pd(dba)$_2$ in the presence of 1 equiv of P(*o*-To)$_3$.[60] In the case of X = C(O)Me, the monomer [Pd{κ^2-*C*,*O*-C_6H_4[C(O)Me}-2}Br{P(*o*-To)$_3$}] (**6c″**), containing a C,O chelate ring instead of a bromo bridging ligand, was obtained, as confirmed by an X-ray diffraction study (see below and Scheme 1). We had already observed the coordination ability of this substituent in (6-acetyl-2,3,4-trimethoxyphenyl)palladium complexes.[17]

The complex **2c** reacts with the alkyne PhC≡CPh or EtC≡CEt and TlOTf to give 1-methyl-2,3-diphenyl-1*H*-indenol (**7**) or 1-methyl-2,3-diethyl-1*H*-indenol (**8**), respectively. The syntheses of these compounds were previously achieved by reacting *ortho*-manganated acetophenone with trimethylamine *N*-oxide and the corresponding alkynes.[33]

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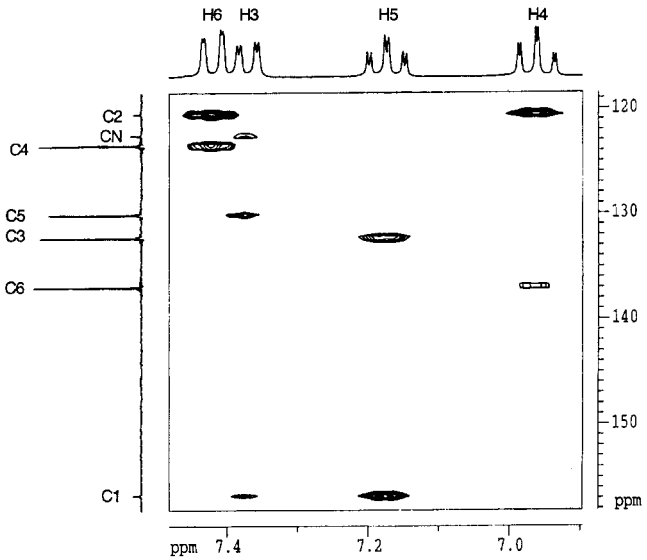

Figure 1. Section of the HMBC spectrum of **2d′**, showing long-range correlations between the ^{13}C signals and the protons of the aryl ligand.

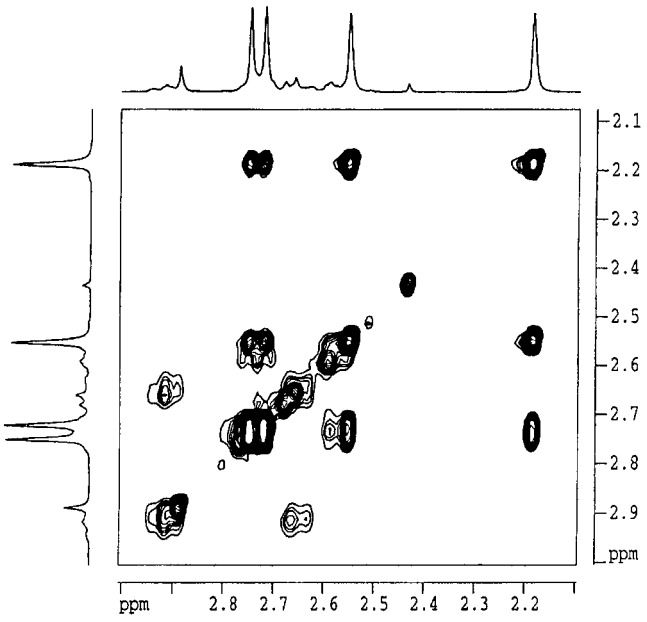

Figure 2. Section of the phase-sensitive ^{1}H-NOESY spectrum of **2b′**, showing exchange cross-peaks among all the methyl groups of the tmeda. The methylene groups are also in mutual exchange.

Spectroscopic Properties of Complexes. The NMR spectra of complexes are in accord with their proposed geometries in Scheme 1. A noteworthy feature of the tmeda complexes **2b′**,**d′** is that they show four resonances corresponding to the Me groups of the tmeda ligand, which indicates a hindered rotation of the aryl groups around the C−Pd bond.[9,19,70] The presence of the vinyl substituent in complexes **1a**,**a′** and **3a** is confirmed in their ^{1}H NMR spectra, which show the signals corresponding to this group with coupling constants of 17−18 (*trans*), 11 (*cis*), and 1 (*gem*) Hz. The formyl derivatives show in their ^{1}H NMR spectra a singlet, assignable to the proton of the formyl group, whose position in **1b** (9.69 ppm) is quite different from that in **2b**, **2b′**, and **5b″** (11.1−11.6 ppm). Probably, in **1b** the magnetic anisotropy induced by one phenyl group of the PPh_3 ligands is responsible for the shielding of the formyl proton (see X-ray Crystal Structures). This difference is not as marked in the ^{13}C NMR spectra (194.54−196.99 ppm). In **2b**,**b′**,**c**,**d**,**d′**, the complete assignment of the NMR resonances of the aryl group has been achieved using ^{13}C,^{1}H one-bond and long-range correlations. As an example, Figure 1 is a section of the HMBC (heteronuclear shift correlations via multiple bond connectivities) spectrum of **2d′**, showing long-range correlations between the ^{13}C signals and the protons of the aryl ligand. These correlations arise from three-bond spin−spin interactions. The CN carbon can be easily distinguished from C-2 because it correlates with just one hydrogen, H-3, while C-2 shows cross-peaks with both H-6 and H-4. In this way, the aryl protons can be fully assigned. Furthermore, it is possible to identify C-3, -4, -5, and -6 from their respective interactions with H-5, -6, -3, and -4. C-1 shows the two expected cross-peaks with H-3 and -5.

A feature of **2c** is that its ^{1}H and ^{13}C NMR room-temperature spectra show a broadening of the signals corresponding to the bpy ligand, whereas the resonances of the aryl ligand appear as sharp signals. The −60 °C ^{1}H NMR spectrum shows the expected signals of the halves of the bpy. The behavior of **5c** is more complex, since its ^{1}H and ^{31}P NMR spectra show broad signals corresponding to both the aryl and the PPh_3 ligands; lowering the temperature to −60 °C causes the sharpening of all signals to give the expected spectra. In **2b′**, a slow fluxional process exchanges all methyl protons of the tmeda ligand (as well as the methylene protons), as shown by its phase-sensitive NOESY spectrum (see Figure 2). In the phase-sensitive NOESY spectrum of **2b** we also observed an exchange of the halves of the bpy. Because these four complexes have a carbonylic function in the *ortho* position of the aryl ligand, we suggest that such fluxional processes involve intermediates in which a change in the coordination mode of the aryl group from monocoordinate to chelate occurs. Such intermediates could be pentacoordinate species and/or square-planar complexes resulting from displacement of the Br ligand to give complexes related to **6c″**. The latter probably exists only in the monomeric form due to steric reasons. The role played by the oxygen in the above fluxional processes seems to be confirmed by the fact that, in the phase-sensitive NOESY spectrum of **2d′**, the exchange in the tmeda ligand, observed in **2b′**, is not detected.

The ^{1}H NMR of complex **5b″** shows three broad signals attributable to the methyl groups of P(*o*-To)$_3$. At −60 °C these signals appear as sharp peaks at 3.61, 1.46, and 0.91 ppm, indicating that rotation around the P−C bonds is hindered; two isomers, *exo*$_3$ (with the three tolyl groups in *exo* positions) and *exo*$_2$ (with one tolyl group in an *endo* position), are accessible, but only the latter is formed. This is confirmed by the presence of a doublet of doublets at 9.59 ppm, assignable to the H6 of the *endo* *o*-To group, which is forced into close proximity to the palladium d_{z^2} orbital. A similar behavior has been observed by Hartwig et al.;[60] however, in our case, the P−Pd bond seems to rotate freely and the three possible rotamers are not observed. Complex **6c″**

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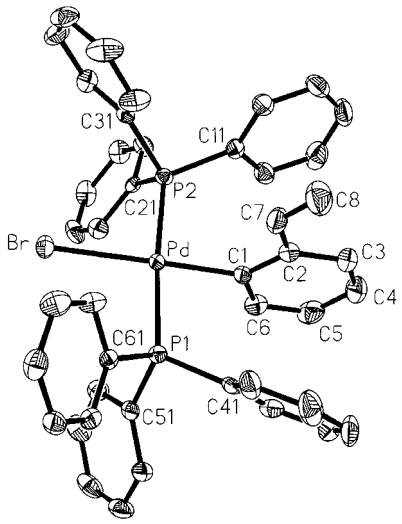

Figure 3. Thermal ellipsoid plot of **1a**·$2CH_2Cl_2$ (50% probability levels) with the labeling scheme. H atoms and solvent are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−C(1) = 2.015(4), Pd−P(1) = 2.3339(11), Pd−P(2) = 2.3266(11), Pd−Br = 2.5462(5), C(2)−C(7) = 1.461(5), C(7)−C(8) = 1.321(6); C(1)−Pd−P(1) = 87.36(11), C(1)−Pd−P(2) = 87.68(11), P(1)−Pd−P(2) = 174.98(4), C(1)−Pd−Br = 174.45(12), P(1)−Pd−Br = 94.64(3), P(2)−Pd−Br = 90.23(3), C(2)−C(7)−C(8) = 127.3(4).

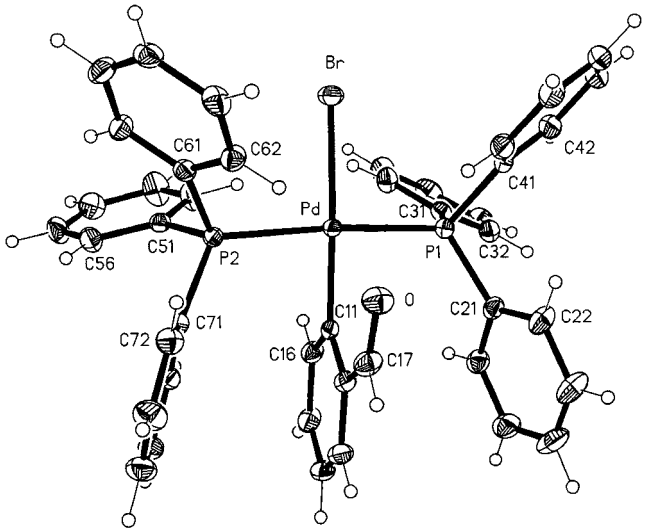

Figure 4. Thermal ellipsoid plot of **1b**·CH_2Cl_2 (50% probability levels) with the labeling scheme. The solvent is omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−C(11) = 1.991(2), Pd−P(1) = 2.3217(6), Pd−P(2) = 2.3243(6), Pd−Br = 2.5029(3), O−C(17) = 1.212(3); C(11)−Pd−P(1) = 87.97(7), C(11)−Pd−P(2) = 86.94(7), P(1)−Pd−P(2) = 173.89(2), C(11)−Pd−Br = 174.43(7), P(1)−Pd−Br = 92.097(17), P(2)−Pd−Br = 92.640(17), O−C(17)−C(12) = 126.5(2).

shows a similar pattern, while **5d″** is not soluble enough for an NMR study.

The IR bands assignable to the ν(CO) mode in **1b**, **2b**,**b′**, **5b**,**b″**, **1c**, **2c**, and **5c** appear in the 1650−1680 cm^{-1} region in the solid state, indicating the noncoordination of the carbonyl group in these complexes. In the case of **1b**, several bands in the 1650−1680 cm^{-1} region are probably attributable to a solid-state effect, since its IR spectrum recorded in dichloromethane solution shows a single band at 1684 cm^{-1}. The compounds **2b**,**b′** and **5b**,**b″** show only one band in the 1682−1692 cm^{-1} region in the solid state. Complexes **4c** and **6c″** have this absorption at lower frequency (1582, 1586 cm^{-1}), which is in accordance with the proposed formulations as C,O palladacycles.

The ν(C≡N) IR bands of the cyanophenyl complexes appear in the region 2212−2220 cm^{-1}.

X-ray Crystal Structures. The crystal and molecular structures (Table 1) of the complexes **1a**·$2CH_2Cl_2$ (Figure 3) **1b**·CH_2Cl_2 (Figure 4), **2b** (Figure 5), **2d** (Figure 6), and **6c″** (Figure 7) have been determined by X-ray diffraction studies. All these complexes show somewhat distorted square planar coordination (mean deviations from the best plane through Pd and the four donor atoms are 0.04, 0.03, 0.06, 0.04, and 0.08 Å, respectively). The distortion may be associated in appropriate cases with the chelating nature of the bpy or the aryl ligand (in **6c″** C(11) lies 0.3 Å out of the plane of Pd, O, P, and Br; mean deviation 0.02 Å).

The Pd−C bond distance in the $C_6H_4(CH{=}CH_2)$-2 complex **1a**·$2CH_2Cl_2$ is significantly longer (2.015(4) Å) than that in the C_6H_4(CHO)-2 complex **1b**·CH_2Cl_2 (1.991(2) Å), despite the otherwise identical ligands. The Pd−C bond distances in the bpy complexes **2b** and **2d** (1.986(4) Å) are similar to those in **1b**·CH_2Cl_2, in turn showing the similarity of (i) bond strength from Pd to the C_6H_4(CHO)-2 and C_6H_4(CN)-2 aryl ligands and (ii)

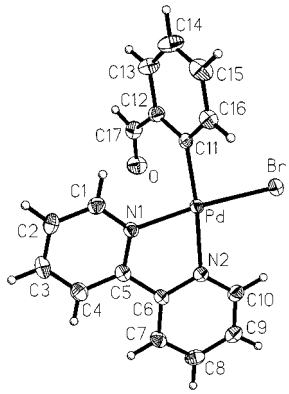

Figure 5. Thermal ellipsoid plot of **2b** (50% probability levels) with the labeling scheme. Selected bond lengths (Å) and angles (deg): Pd−C(11) = 1.986(4), Pd−N(1) = 2.060(3), Pd−N(2) = 2.108(3), Pd−Br = 2.4207(6), O−C(17) = 1.204(5); C(11)−Pd−N(1) = 95.8(2), C(11)−Pd−N(2) = 174.1(2), N(1)−Pd−N(2) = 79.18(13), C(11)−Pd−Br = 88.96(11), N(1)−Pd−Br = 173.79(9), N(2)−Pd−Br = 96.28(9), O−C(17)−C(12) = 127.3(4).

trans influence of the Br and bpy ligands. The Pd−C bond distance in the C_6H_4{C(O)Me}-2 complex **6c″** (2.021(2) Å) is similar to that in **1a**·$2CH_2Cl_2$.

The Pd−Br bond lengths follow the order **1a**·$2CH_2Cl_2$ (2.5462(5) Å) > **6c″** (2.5085(3) Å) ≈ **1b**·CH_2Cl_2 (2.5029(3) Å) > **2b** (2.4207(6) Å) > **2d** (2.4127(6) Å), showing the scale of *trans* influence: $C_6H_4(CH{=}CH_2)$-2 > C_6H_4{C(O)Me}-2 ≈ C_6H_4(CHO)-2 ≫ bpy. The shortening of the Pd−Br bond in **2d** with respect to **2b** could be associated with the intermolecular hydrogen bond between the bromo ligand and H(11A) of the bpy ligand in **2d** (see below). The Pd−N bond distances in complexes **2b** (Pd−N *trans* to aryl, 2.108(3) Å; Pd−N *trans* to Br, 2.060(3) Å) and **2d** (Pd−N *trans* to aryl, 2.112(3) Å; Pd−N *trans* to Br, 2.056(3) Å) show the scale of *trans* influence: C_6H_4(CHO)-2 = C_6H_4CN-2 ≫ bpy. The Pd−P

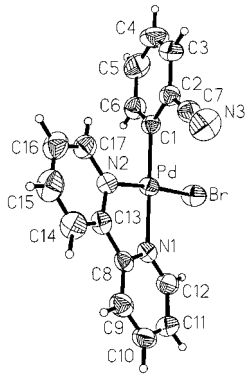

Figure 6. Thermal ellipsoid plot of **2d** (50% probability levels) with the labeling scheme. Selected bond lengths (Å) and angles (deg): Pd−C(1) = 1.986(4), Pd−N(1) = 2.112(3), Pd−N(2) = 2.056(3), Pd−Br = 2.4127(6), C(7)−N(3) = 1.140(5); C(1)−Pd−N(1) = 173.37(13), C(1)−Pd−N(2) = 95.66(13), N(1)−Pd−N(2) = 79.21(12), C(1)−Pd−Br = 88.76(10), N(1)−Pd−Br = 96.41(8), N(2)−Pd−Br = 175.57(9), N(3)−C(7)−C(2) = 179.1(5).

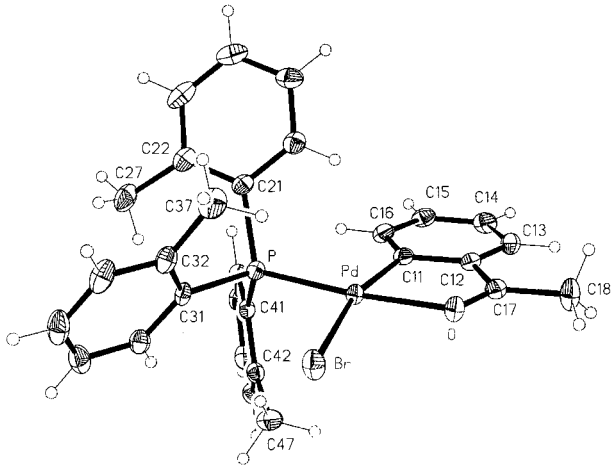

Figure 7. Thermal ellipsoid plot of **6c″** (50% probability levels) with the labeling scheme. Selected bond lengths (Å) and angles (deg): Pd−C(11) = 2.021(2), Pd−O = 2.1103(15), Pd−P = 2.2546(6), Pd−Br = 2.5085(3), O−C(17) = 1.242(3); C(11)−Pd−O = 80.84(8), C(11)−Pd−P = 95.81(7), O−Pd−P = 175.11(5), C(11)−Pd−Br = 166.03(7), O−Pd−Br = 86.96(4), P−Pd−Br = 96.765(18), C(17)−O−Pd = 113.57(15), C(12)−C(17)−O = 118.5(2).

bond distances in complexes **1a**·2CH_2Cl_2 and **1b**·CH_2Cl_2 (2.3339(11)−2.3217(6) Å) are significantly longer than in **6c″** (2.2546(6) Å). With all the above data, the following scale of trans influence results: C_6H_4(CH=CH_2)-2 > C_6H_4{C(O)Me}-2 ≥ C_6H_4(CHO)-2 = C_6H_4CN-2 ≫ bpy = Br; PPh_3 > O=C(Me)C_6H_4-2.

The crystal structure of **6c″** confirms the monomeric structure proposed for this complex, based on the C,O chelating nature of the aryl ligand, and also the exo_2 conformation of the phosphine deduced by ^{1}H NMR spectroscopy. The coordination of the carbonylic oxygen leads to a slight lengthening of the C=O bond (1.242(3) Å) with respect to the mean value in ketones (1.221 Å).[71]

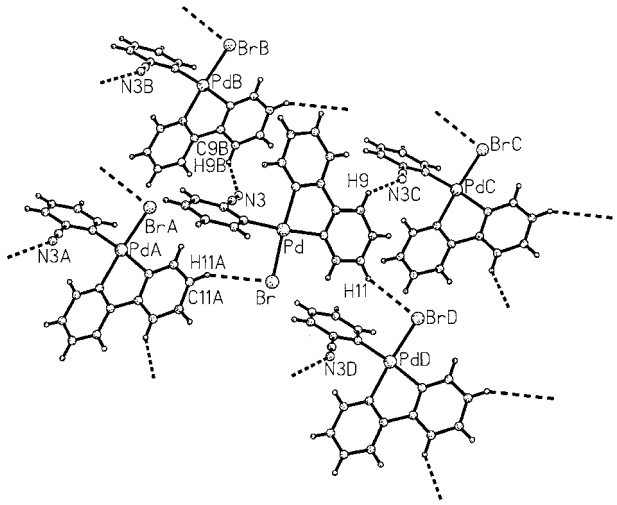

Figure 8. Hydrogen bond interactions in **2d**.

In the complexes **1b**·CH_2Cl_2 and **2b**, the O atom of the formyl group makes a short contact of 2.884(2) or 2.982(3) Å to the Pd atom, but the C=O bond lengths are normal (1.212(3) and 1.204(5) Å, respectively). X-ray diffraction and NMR studies by Pregosin et al. have shown that, in some (quinoline-8-carbaldehyde)platinum complexes, the CHO group interacts with the metal through the H atom.[72,73]

In complex **2d**, the molecules are connected to form layers through intermolecular CN···H−C_{bpy} and Br···H−C_{bpy} hydrogen bonds (N(3)···H(9B), 2.51 Å; N(3)···C(9B), 3.243(5) Å; N(3)···H(9B)−C(9B), 150°; Br···H(11A), 3.01 Å; Br···C(11A), 3.845(4) Å; N(3)···H(9B)−C(9B), 136°). As shown in Figure 8, each molecule uses its Br and N atoms and the pair of H atoms of the pyridine ring *trans* to the aryl ligand, H(9) and H(11), to form hydrogen bonds with H(11), H(9), N, and Br atoms, respectively, of four neighboring molecules.

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Supporting Information Available: Tables giving crystal data and refinement details, atomic coordinates and thermal parameters, and bond distances and angles for **1a**·2CH_2Cl_2, **1b**·CH_2Cl_2, **2b**, **2d**, and **6c″**. This material is available free of charge via the Internet at http://pubs.acs.org.

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