Synthesis of Palladium Complexes with ortho-Functionalized Aryl Ligands

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The complexes $[Pd(C_6H_4X-2)BrL_2]$ (L₂ = trans-(PR₃)₂, R = Ph, X = CH=CH₂ (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" (=[Pd₂(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 $[Pd{\kappa^2-C, O-C_6H_4{C(O)Me}-2}(bpy)]TfO (4c)$ has been prepared from 2c and TIOT f. The dimeric complexes $[Pd(\mu-Br)(C_6H_4X-2)(PR_3)]_2$ (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 $[Pd{\kappa^2-C, O-C_6H_4}(C(O)Me]-2]Br{P(o-To)_3}]$ (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·2CH₂Cl₂, 1b·CH₂Cl₂, 2b,d, and 6c" have been determined by X-ray diffraction studies. An interesting supramolecular layered structure is formed through $CN \cdots H - C_{bpy}$ 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 CO13,14 and other unsaturated reagents.¹⁵ Thus, we have prepared complexes containing aryl groups such as C₆H(OMe)₃-3,4,5-CHO-2, $C_6H(OMe)_3$ -2,3,4-X-6 (X = CHO, C(O)Me, CH₂OEt, C(O)NHBu^t),^{12,16-18} and C₆H₃(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 catalyst²⁰⁻²³ 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-CHOaryl)- 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 (2,3,4trimethoxy-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 $Pd{C_6H_4CN}$ -2Cl(PPh₃)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

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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" ([Pd₂-(dba)₃]·dba, dba = dibenzylideneacetone)^{1,31} and [PdCl₂-(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{C₆H₄(CH=CH₂)-2}Br(PPh₃)₂] (1a). "Pd(dba)₂" (150 mg, 0.26 mmol), PPh₃ (137 mg, 0.52 mmol), and 2-bromostyrene (51 μ L, 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 MgSO4. 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 C44H37BrP2Pd: C, 64.92; H, 4.58. Found: C, 64.93; H, 4.50. ¹H NMR (300 MHz, CDCl₃): δ 7.8-7.15 (several m, 30H, PPh₃), 6.97 (dd, 1H, CH=CH₂, ${}^{3}J_{HH} =$ 17 Hz, ${}^{3}J_{HH} = 11$ Hz), 6.91–6.86 (m, 1H, C₆H₄), 6.47–6.42 (m, 2H, C₆H₄), 6.28-6.23 (m, 1H, C₆H₄), 5.20 (dd, 1H, CH=CH₂ *trans* to H, ${}^{2}J_{HH} = 1$ Hz, ${}^{3}J_{HH} = 17$ Hz), 4.84 (dd, 1H, CH= $CH_2 cis$ to H, ${}^2J_{HH} = 1$ Hz, ${}^3J_{HH} = 11$ Hz). ${}^{13}C$ NMR (50 MHz, CDCl₃): δ 158.28 (t, C-Pd C₆H₄, ²J_{PC} = 3 Hz), 142.04 (t, *C*-CH=CH₂, ${}^{3}J_{PC} = 3$ Hz), 141.08 (t, *C*H=CH₂, ${}^{4}J_{PC} = 2$ Hz), 135.63 (t, C6 C₆H₄, ${}^{3}J_{PC} = 5$ Hz), 134,70 (t, *ortho* C's PPh₃, J_{PC} = 6 Hz), 131,27 (t, *ipso* C's PPh₃, $J_{PC} = 23$ Hz), 129.66 (s, *para* C's PPh₃), 127.69 (t, meta C's PPh₃, $J_{PC} = 5$ Hz), 126.71 (s, CH C₆H₄), 126.06 (s, CH C₆H₄), 122.67 (s, CH C₆H₄), 111.64 (s, CH₂). ³¹P NMR (121 MHz, CDCl₃): δ 22.87 (s).

Synthesis of *trans*-[Pd{C₆H₄(CH=CH₂)-2}Br{P(p-To)₃}₂] (1a'). Complex 1a' was similarly prepared from "Pd(dba)₂" (150 mg, 0.26 mmol), $P(p-T_0)_3$ (p-T_0 = 4-tolyl; 159 mg, 0.52 mmol), and 2-bromostyrene (51 μ L, 0.39 mmol). Color: pale brown. Yield: 160 mg, 68%. Mp: 138 °C dec. Anal. Calcd for C₅₀H₄₉-BrP₂Pd: C, 66.86; H, 5.50. Found: C, 66.70; H, 5.46. ¹H NMR (300 MHz, CDCl₃): 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=CH₂, H trans to H, ${}^{2}J_{HH} = 1$ Hz, ${}^{3}J_{HH} = 17$ 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). ¹³C NMR (50 MHz, CDCl₃): δ 158,87 (t, C-Pd, ²J_{PC} = 3 Hz), 142.00 (t, C-CH=CH₂, ${}^{3}J_{PC} = 3$ Hz), 141.42 (t, CH=CH₂, ⁴J_{PC} = 2 Hz), 139.48 (s, para C's P(p-To)₃), 135.60 (t, C6 C₆H₄, ${}^{3}J_{PC} = 5$ 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 C₆H₄), 125.84 (s, CH C₆H₄), 122.17 (s, CH C₆H₄), 119.29 (s, CH₂), 21.36 (s, Me). ³¹P NMR (121 MHz, CDCl₃): δ 21.01 (s).

Synthesis of *trans*-[Pd{C₆H₄(CHO)-2}Br(PPh₃)₂] (1b). Complex 1b was similarly prepared from "Pd(dba)₂" (150 mg, 0.26 mmol), PPh₃ (137 mg, 0.52 mmol), and 2-bromobenzaldehyde (45 μ L, 0.39 mmol). Color: pale yellow. Yield: 168 mg, 79%. Mp: 184 °C dec. Anal. Calcd for C₄₃H₃₅BrOP₂Pd: C, 63.29; H, 4.32. Found: C, 63.22; H, 4.36. ¹H NMR (300 MHz, CDCl₃): δ 9.69 (s, 1H, CHO), 7.55–6.58 (several m, 34 H, PPh₃ and C₆H₄). ¹³C NMR (50 MHz, CDCl₃): δ 194.54 (s, CHO), 168.52 (t, C–Pd, ²J_{PC} = 4 Hz), 140.07 (s, *C*-CHO), 135.14 (t, C6 C₆H₄, ³J_{PC} = 4 Hz), 134.51 (t, *ortho* C's PPh₃, J_{PC} = 6 Hz), 133.04 (s, CH C₆H₄), 131.09 (s, CH C₆H₄), 130.71 (t, *ipso* C's PPh₃, J_{PC} = 5 Hz), 122.51 (s, C4 C₆H₄). ³¹P NMR (121 MHz,

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CDCl₃): δ 23.17 (s). IR (cm⁻¹): ν (CO) 1682 (solid) 1684 (dichloromethane solution).

Synthesis of trans- $[Pd{C_6H_4{C(0)Me}-2}Br(PPh_3)_2]$ (1c). "Pd(dba)2" (200 mg, 0.35 mmol), PPh3 (184 mg, 0.70 mmol), and 2-bromoacetophenone (71 μ L, 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 \times 10 mL), and the combined extracts were filtered over anhydrous MgSO₄. 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 C44H37BrOP2Pd: C, 63.67; H, 4.49. Found: C, 63.40; H, 4.80. ¹H NMR (300 MHz, CDCl₃; -60 °C): δ 7.60-7.17 (several m, 31H), 6.76 (d, 1H, C₆H₄, ${}^{3}J_{HH} = 7$ Hz), 6.65 (t, 1H, C₆H₄, ${}^{3}J_{\rm HH}$ = 7 Hz), 6.57 (t, 1H, C₆H₄, ${}^{3}J_{\rm HH}$ = 7 Hz), 1.76 (s, 3H, Me). ¹³C NMR (50 MHz, CDCl₃): δ 198.40 (s, CO), 165.68 (s, C-Pd), 141.04 (s, CC(O)Me), 135.32 (bs, C6 C₆H₄), 134.67 (t, ortho C's PPh₃, $J_{PC} = 5$ Hz), 133.24 (s, CH C₆H₄), 131,26 (t, *ipso* C's PPh₃, J_{PC} = 22 Hz), 129.50 (s, *para* C's PPh₃), 127.68 (bs, meta C's PPh₃), 121.83 (s, CH C₆H₄), 26.76 (s, Me). ³¹P NMR (121 MHz, CDCl₃): δ , 23.05 (s). IR (cm⁻¹): ν (CO) 1660 (Nujol).

Synthesis of *trans*-[Pd{C₆H₄(CN)-2}Br(PPh₃)₂] (1d). Complex 1d was prepared as described for 1a from "Pd(dba)₂" (150 mg, 0.26 mmol), PPh₃ (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 C₄₃H₃₄NP₂Pd: C, 63.53; H, 4.22; N, 1.72. Found: C, 63.28; H, 4.36; N, 1.64. ¹H NMR (300 MHz, CDCl₃): δ 7.7–7.1 (several m, 31 H), 6.61–6.55 (m, 1H), 6.41–6.39 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 167.14 (t, C–Pd, ²J_{PC} = 5 Hz), 135.67 (t, C6 C₆H₄, ³J_{PC} = 4 Hz), 134,68 (t, *ortho* C's PPh₃, J_{PC} = 6 Hz), 132.84 (s, CH C₆H₄), 130.61 (t *ipso* C's PPh₃, J_{PC} = 23 Hz), 129.94 (s, *para* C's PPh₃), 129.71 (s, CH C₆H₄), 127.91 (t, *meta* C's PPh₃, J_{PC} = 5 Hz), 122.20 (s, C4 C₆H₄), 121.79 (s, CN), 120.29 (t, *C*-CN, ³J_{PC} = 4 Hz). ³¹P NMR (121 MHz, CDCl₃): δ 23.32 (s). IR (cm⁻¹): ν (CN) 2212 (Nujol).

Synthesis of [Pd{C₆H₄(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 μ L, 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 C₁₇H₁₃BrN₂OPd: C, 45.62; H, 2.93; N, 6.26. Found: C, 45.74; H, 2.84; N, 6.10. ¹H NMR (200 MHz, CDCl₃): δ 11.09 (s, 1H, CHO), 9.42 (d, 1H, H6' bpy, ${}^{3}J_{\rm HH} = 5$ Hz), 8.14-8.05 (several m, 3H, H3, H3' and H4' bpy), 8.00 (td, 1H, H4 bpy, ${}^{3}J_{\text{HH}} = 8$ Hz, ${}^{4}J_{\text{HH}} = 2$ Hz), 7.78 (dd, 2H, aryl H3 and H6, ${}^{3}J_{\text{HH}} = 8$ Hz, ${}^{4}J_{\text{HH}} = 1$ Hz), 7.64–7.57 (m, 1H, H5' bpy), 7.52 (dd, 1H, H6 bpy, ${}^{3}J_{HH} = 6$ Hz, ${}^{4}J_{HH} = 1$ Hz), 7.31– 7.21 (m, 2H, aryl H5 and H5 bpy), 7.09 (t, 1H, aryl H4, ${}^{3}J_{\rm HH}$ = 7 Hz). ¹³C NMR (50 MHz, CDCl₃): 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 C₆H₄), 131.97 (s, C5 C₆H₄), 128.30 (s, C3 C₆H₄), 126.81 (b s, C5 and 5' bpy), 124.02 (s, C4 C₆H₄), 122.40 (s, C3 bpy), 121.67 (s, C3' bpy). IR (cm⁻¹): ν (CO) 1682 (Nujol).

Synthesis of [Pd{C₆H₄(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 μ L, 0.26 mmol), and 2-bromobenzaldehyde (45 μ L, 0.39 mmol). Color: yellow. Yield: 76 mg, 72%. Mp: 181 °C dec. Anal. Calcd for C₁₃H₂₁-BrN₂OPd: C, 38.31; H, 5.19; N, 6.87. Found: C, 38.51; H, 5.23; N, 6.89. ¹H NMR (200 MHz, CDCl₃): 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 ×

CH₂), 2.73 (s, 3H, Me), 2.70 (s, 3H, Me), 2.53 (s, 3H, Me), 2.17 (s, 3H, Me).¹³C NMR (50 MHz, CDCl₃): 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, CH₂), 58.45 (s, CH₂), 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{C₆H₄{C(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 C₁₈H₁₅BrN₂OPd: C, 46.83; H, 3.27; N, 6.07. Found: C, 46.68; H, 3.17; N, 5.90. ¹H NMR (300 MHz, CDCl₃; -60 °C): δ 9.45 (d, 1H, bpy, ${}^{3}J_{\text{HH}} = 5$ Hz), 8.14 (m, 3H), 8.05 (t, 1H, ${}^{3}J_{HH} = 8$ Hz), 7.83 (t, 2H, $J_{HH} = 8$ Hz), 7.63 (t, 1H, $J_{\rm HH} = 6$ Hz), 7.57 (d, 1H, $J_{\rm HH} = 6$ Hz), 7.35–7.23 (m, 2H), 7.13 (t, 1H, $J_{\rm HH} = 7$ Hz), 2.86 (s, 3H, Me). ¹³C NMR (50 MHz, CDCl₃): 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 C₆H₄), 129.96 (s, C5 C₆H₄), 129.71 (s, C3 C₆H₄), 126.57 (b s, C5 and 5' bpy), 123.30 (s, C4 C₆H₄), 121.70 (b s, C3 and 3' bpy), 30.30 (s, Me). IR (cm⁻¹): ν (CO) 1660 (Nujol).

Synthesis of [Pd{C₆H₄(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 \times 10 mL). The combined extracts were filtered over anhydrous MgSO₄, 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 C₁₇H₁₂BrN₃Pd: C, 45.93; H, 2.72; N, 9.45. Found: C, 45.80; H, 2.45; N, 9.11. ¹H NMR (200 MHz, CDCl₃): δ 9.16 (d, 1H, H6' bpy, ${}^{3}J_{\text{HH}} = 5$ Hz), 8.69–8.63 (m, 2H, H3 and H3' bpy), 8.30 (dt, 2H, H4 and 4' bpy, $J_{\rm HH} =$ 7 Hz, $J_{\rm HH} = 1$ Hz), 7.84 (t, 1H, H5' bpy, $J_{\rm HH} = 6$ Hz), 7.65 (t, 1H, H5 bpy, $J_{\rm HH} = 6$ 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, $J_{\rm HH}$ = 7 Hz). ¹³C NMR (50 MHz, *d*₆-dimethyl sulfoxide): δ 156.24 (s, C1 C₆H₄), 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 C₆H₄), 132.38 (s, C3 C₆H₄), 130.21 (s, C5 C₆H₄), 127.70 (s, C5 bpy), 127.37 (s, C5' bpy), 123.98 (s, C3 bpy), 123.89 (s, C4 C₆H₄), 123.25 (s, C3' bpy), 121.41 (s, CN), 118.88 (s, C-CN). IR (cm⁻¹): v(CN) 2218 (Nujol).

Synthesis of [Pd{C₆H₄(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 C₁₃H₂₀BrN₃Pd: C, 38.59; H, 4.98; N, 10.38. Found: C, 38.67; H, 4.84; N, 9.91. ¹H NMR (200 MHz, CDCl₃): δ 7.40 (dd, 1H, H6, ${}^{3}J_{HH} = 8$ Hz, ${}^{4}J_{HH} = 1$ Hz), 7.34 (dd, 1H, H3, ${}^{3}J_{HH} = 8$ Hz, ${}^{4}J_{\rm HH} = 2$ Hz), 7.13 (td, 1H, H5, ${}^{3}J_{\rm HH} = 8$ Hz, ${}^{4}J_{\rm HH} = 2$ Hz), 6.91 (td, 1H, H4, ${}^{3}J_{HH} = 8$ Hz, ${}^{4}J_{HH} = 1$ Hz), 3.0–2.3 (m, 4H, 2 × CH₂), 2,74 (s, 3H, Me), 2.66 (s, 3H, Me), 2.56 (s, 3H, Me), 2.46 (s, 3H, Me). ¹³C NMR (50 MHz, d_6 -CDCl₃): 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, CCN), 62.45 (s, CH₂), 58.34 (s, CH₂), 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). TIOTf (TfO = CF₃SO₃; 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. $\Lambda_{\rm M}$ (acetone): 116 Ω^{-1} cm² mol⁻¹. Anal. Calcd for C₃₇H₃₀F₃N₂O₃PdS: 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. ¹H NMR (300 MHz, CDCl₃): 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=CH₂ H *trans* to H, ³J_{HH} = 18 Hz, ²J_{HH} = 1 Hz), 5.04 (dd, 1H, CH=CH₂ H *cis* to H, ³J_{HH} = 11 Hz, ²J_{HH} = 1 Hz). ³¹P NMR (121 MHz, CDCl₃): δ 32.61 (s).

Synthesis of [Pd{ κ^2 -*C*,*O*-C₆H₄{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} cm² mol⁻¹. NMR: not sufficiently soluble. Anal. Calcd for C₁₉H₁₅F₃N₂O₃-PdS: 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 $[Pd_2(\mu-Br)_2\{C_6H_4(CHO)-2\}_2(PPh_3)_2]$ (**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 C₅₀H₄₀Br₂O₂P₂Pd₂: C, 54.23; H, 3.64. Found: C, 53.90; H, 3.34. IR (cm⁻¹): ν (C=O) 1692 (Nujol).

Synthesis of $[Pd_2(\mu-Br)_2\{C_6H_4(CHO)-2\}_2\{P(o-To)_3\}_2]$ (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 \times 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 airdried to give 5b" as a yellow solid. Yield: 82 mg, 53%. Mp: 210 °C dec. Anal. Calcd for (C28H26BrOPPd)2: C, 56.45; H, 4.40. Found: C, 56.54; H, 4.14. ¹H NMR (300 MHz, CDCl₃, -60 °C): δ 11.60 (bs, 1H, CHO), 9.59 (dd, 1H, H6 o-To endo, ³J_{PH} = 19 Hz, ${}^{3}J_{\text{HH}}$ = 7 Hz), 7.9–6.5 (several m, 15H), 3.61 (s, 3H, Me), 1.46 (s, 3H, Me), 0.91 (s, 3H, Me). ³¹P NMR (121 MHz, CDCl₃, -60 °C): δ 27.83 (s). IR (cm⁻¹): ν (C=O) 1682 (Nujol).

Synthesis of $[Pd_2 (\mu-Br)_2 \{C_6H_4 \{C(0)Me\}-2\}_2 (PPh_3)_2]$ (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 C₅₂H₄₄Br₂O₂P₂Pd₂: C, 55.01; H, 3.91. Found: C, 54.83; H, 3.96. ¹H NMR (300 MHz, CDCl₃, -60 °C): δ 7.8–7.2 (several m, 16H), 7.08 (t, 1H, C₆H₄, J_{HH} = 7 Hz), 6.83 (t, 1H, C₆H₄, J_{HH} = 7 Hz), 6.38 (t, 1H, C₆H₄, J_{HH} = 7 Hz), 2.81 (s, 3H, Me). ³¹P NMR (121 MHz, CDCl₃, -60 °C): δ 49.64 (s). IR (cm⁻¹): ν (C=O) 1660 (Nujol).

Synthesis of $[Pd_2(\mu-Br)_2\{C_6H_4(CN)-2\}_2(PPh_3)_2]$ (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 $[Pd_2(\mu$ -Br)₂{ $C_6H_4(CN)-2$ }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 (C₂₈H₂₅BrNPPd)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{ k^2 -*C*,*O*-C₆H₄{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 μ L, 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 \times 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. ¹H NMR (300 MHz, CDCl₃): δ 8.70 (dd, 1H, H6 endo o-To, ${}^{3}J_{\rm PH} = 18$ Hz, ${}^{3}J_{\rm HH} = 8$ Hz), 7.5–7.1 (several m, 11H), 6.98 (t, 1H, $J_{\rm HH} = 7$ Hz), 6.76 (t, 1H, $J_{\rm HH} = 7$ Hz), 6.49 (t, 1H, $J_{\rm HH} =$ 7 Hz), 3.27 (s, 3H, Me), 2.71 (s, 3H, COMe), 2.09 (s, 3H, Me), 1.68 (s, 3H, Me). ³¹P NMR (121 MHz, CDCl₃): δ 38.37 (s). Anal. Calcd for C₂₉H₂₈BrOPPd: 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 cm³, 0.88 mmol) and TlOTf (156 mg, 0.44 mmol) were added to a solution of **2c** (200 mg, 0.44 mmol) in 15 cm³ of CH₂Cl₂. 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/CH₂Cl₂ as eluant. The first, colorless band was taken. The product was extracted with acetone, stirred with anhydrous MgSO₄, 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-CH₂Cl₂ 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 K α 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**· CH₂Cl₂ the dichloromethane molecule is disordered over an inversion center.

Compounds 1a·2CH₂Cl₂, 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.

$\mathbf{A} \mathbf{A} \mathbf{A} \mathbf{A} \mathbf{A} \mathbf{A} \mathbf{A} \mathbf{A} $	Table 1.	Crystal D	Data for	1a·2CH ₂ C	l _s . 1b·CF	I ₂ Cl ₂ , 2	2b. 2d.	and 6c
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	$1a \cdot 2CH_2Cl_2$	$1b \cdot CH_2Cl_2$	2b	2d	6c″
formula	C46H41BrCl4P2Pd	C43 5H36BrClOP2Pd	C ₁₇ H ₁₃ BrN ₂ OPd	C ₁₇ H ₁₂ BrN ₃ Pd	C29H28BrOPPd
M _r	959.88	858.42	447.61	444.61	609.79
source	vapor diffusion	liquid diffusion	liquid diffusion	liquid diffusion	liquid diffusion
	hexane/CH ₂ Cl ₂	hexane/CH ₂ Cl ₂	hexane/CH ₂ Cl ₂	hexane/CH ₂ Cl ₂	hexane/CH ₂ Cl 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)
<i>b</i> , Å	28.951(2)	18.9947(16)	13.5645(13)	13.799(2)	12.9761(10)
<i>c</i> , 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
<i>V</i> , Å ³	4341.3	3658.8	1532.9	1599.3	5022.3
Ζ	4	4	4	4	8
radiation used	Μο Κα	Μο Κα	Μο Κα	Μο Κα	Μο Κα
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
<i>Т</i> , К	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 imes 0.32 imes 0.28	$0.33 \times 0.20 \times 0.17$	$0.60\times0.20\times0.14$	$0.42\times0.20\times0.14$	$0.20\times0.17\times0.06$
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
<i>hkl</i> 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
$R_{\rm int}$	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 = $\sum ||F_0| - |F_c||\sum |F_0|$ for reflections with $I > 2\sigma(I)$. ^{*b*} wR2 = $\left[\sum [w(F_0^2 - F_c^2)^2 / \sum [w(F_0^2)^2]\right]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_0^2)/3$ 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**·2CH₂Cl₂ 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", PR₃, and 2-bromostyrene in an 1:2:1.5 molar ratio led to the complexes *trans*-[Pd(C₆H₄X-2)Br(PR₃)₂] (X = CH=CH₂, 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(PPh₃)₄] instead of the mixture "Pd(dba)₂" + PR₃.

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 PPh₃ were successful, yielding *trans*-[Pd(C₆H₄X-2)Br(PR₃)₂] (R = Ph, X = CHO (**1b**), C(O)Me (**1c**), CN (**1d**)), as were those using bpy or tmeda, giving the complexes *cis*-[Pd(C₆H₄X-2)Br(L₂)] (L₂ = bpy, X = CHO (**2b**), C(O)Me (**2c**), CN (**2d**); L₂ = tmeda, X = CHO (**2b**'), CN (**2d**')). It was not possible to obtain the complex [Pd(C₆H₄C(O)Me-2)-Br(tmeda)].

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

The complexes $[Pd(Ar)(\mu - X)]_2$ (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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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-

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 $(C_6H_4X-2)(\mu-Br)(PR_3)]_2$. 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 PPh₃ 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 ¹H NMR spectrum of the product of the reaction. Nevertheless, it was possible to prepare the desired complexes $[Pd(C_6H_4X-2)(\mu-Br) (PPh_3)_2$ (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 PhCH₂C(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 PPh₃ and the aryl ligand, which is a very well-known process.^{62–67} In contrast, the homologous complexes [Pd(C₆H₄X-2)- $(\mu$ -Br){P(o-To)₃]₂ (X = CHO (**5b**''), CN = (**5d**'')) were prepared by oxidative addition reactions of BrC₆H₄X-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 $[Pd{\kappa^2-C, O-C_6H_4{C(O)Me}-2}Br{P(o-T_0)_3}]$ (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 ¹³C signals and the protons of the aryl ligand.

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 ¹H 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 ¹H 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 PPh₃ ligands is responsible for the shielding of the formyl proton (see X-ray Crystal Structures). This difference is not as marked in the ¹³C 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 ¹³C,¹H 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 ¹³C 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 crosspeaks with H-3 and -5.

A feature of **2c** is that its ¹H and ¹³C NMR roomtemperature 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



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

¹H NMR spectrum shows the expected signals of the halves of the bpy. The behavior of 5c is more complex, since its ¹H and ³¹P NMR spectra show broad signals corresponding to both the aryl and the PPh₃ 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 ¹H 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 $1a \cdot 2CH_2Cl_2$ (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).

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 $1a \cdot 2CH_2Cl_2$ (Figure 3) $1b \cdot CH_2Cl_2$ (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 C₆H₄(CH=CH₂)-2 complex **1a**·2CH₂Cl₂ is significantly longer (2.015(4) Å) than that in the C₆H₄(CHO)-2 complex **1b**·CH₂Cl₂ (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**·CH₂Cl₂, in turn showing the similarity of (i) bond strength from Pd to the C₆H₄(CHO)-2 and C₆H₄(CN)-2 aryl ligands and (ii)



Figure 4. Thermal ellipsoid plot of $1b \cdot CH_2Cl_2$ (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).



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 $C_6H_4\{C(0)Me\}-2$ complex **6c**" (2.021(2) Å) is similar to that in **1a**·2CH₂Cl₂.

The Pd–Br bond lengths follow the order $1a \cdot 2CH_2$ -Cl₂ (2.5462(5) Å) > **6c**'' (2.5085(3) Å) $\approx 1b \cdot CH_2Cl_2$ (2.5029(3) Å) > **2b** (2.4207(6) Å) > **2d** (2.4127(6) Å), showing the scale of *trans* influence: C₆H₄(CH=CH₂)-2 > C₆H₄{C(O)Me}-2 $\approx C_6H_4(CHO)-2 \gg$ 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: C₆H₄(CHO)-2 = C₆H₄CN-2 \gg 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 **6**c'' (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 $1a \cdot 2CH_2Cl_2$ and $1b \cdot CH_2$ -Cl₂ (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: C₆H₄(CH= CH₂)-2 > C₆H₄{C(O)Me}-2 ≥ C₆H₄(CHO)-2 = C₆H₄CN-2 \gg bpy = Br; PPh₃ > O=C(Me)C₆H₄-2.

The crystal structure of **6**c'' confirms the monomeric structure proposed for this complex, based on the C,O chelating nature of the aryl ligand, and also the exo₂ conformation of the phosphine deduced by ¹H 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**·CH₂Cl₂ 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 $\text{CN} \cdot \text{H} - \text{C}_{\text{bpy}}$ and $\text{Br} \cdot \text{H} - \text{C}_{\text{bpy}}$ hydrogen bonds (N(3) $\cdot \cdot \text{H}(9\text{B})$, 2.51 Å; N(3) $\cdot \cdot \text{C}(9\text{B})$, 3.243(5) Å; N(3) $\cdot \cdot \text{H}(9\text{B}) - \text{C}(9\text{B})$, 150°; $\text{Br} \cdot \text{H}(11\text{A})$, 3.01 Å; $\text{Br} \cdot \cdot \text{C}(11\text{A})$, 3.845(4) Å; N(3) $\cdot \cdot \text{H}(9\text{B}) -$ 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**· 2CH₂Cl₂, **1b**·CH₂Cl₂, **2b**, **2d**, and **6c**["]. This material is available free of charge via the Internet at http://pubs.acs.org.

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