Palladium-Assisted Formation of Carbon−Carbon Bonds. 9.† Synthesis of (2-Alkenylaryl)- and Indenylpalladium Complexes

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(*o*-Formylaryl)palladium complexes [Pd{C_6H(CHO)-6-R_3-2,3,4}X(N−N)] [R = OMe; X = Cl; N−N = bpy (2,2′-bipyridine) (1a), tmeda (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) (**1b**). R = H; X = Br; N−N = bpy (**2a**), tmeda (**2b**)] react with ylides $PhCH{=}PPh_3$, $pyCH{=}PPh_3$ (py = 2-pyridyl), or $ClCH{=}PPh_3$ to give the (*o*-alkenylaryl)palladium derivatives [Pd{C_6-HCH=CHPh-6-$(OMe)_3$-2,3,4}Cl(N−N)] [N−N = bpy (**3a**), N−N = tmeda (**3b**)], [Pd{C_6HCH=CHpy-6-$(OMe)_3$-2,3,4}Cl(N−N)] [N−N = bpy (**4**)], [Pd{C_6H(*E*-CH=CHCl)-6-$(OMe)_3$-2,3,4}-Cl(tmeda)] (**5**), or [Pd(C_6H_4CH=CHPh-2)Br(N−N)] [N−N = bpy (**6a**), N−N = tmeda (**6b**)]. The compounds **3a**, **4**, and **6a,b** are obtained as mixtures of *E* and *Z* isomers, whereas the formation of **3b** and **5** is stereoselective (*E* isomer). The reaction of the (*o*-acetylaryl)palladium complexes [Pd{$C_6HC(O)Me$-6-$(OMe)_3$-2,3,4}Cl(tmeda)] (**7**) and [Pd{C_6H_4(C(O)Me)-2}Br(bpy)] (**8**) with bases results in the formation of the 3-palladaindan-1-ones [Pd(κ^2-{$C_6HC(O)CH_2$-6-$(OMe)_3$-2,3,4})(tmeda)] (**9**) and [Pd(κ^2-{$C_6H_4C(O)CH_2$-2}(bpy)] (**10**). Complexes **3b** and **6a,b** react with alkynes RC≡CR′ to give indenylpalladium complexes [Pd{η-C_9HBn-1-R-2-R′-3-$(OMe)_3$-5,6,7}(tmeda)]TfO [Bn = benzyl, TfO = CF_3SO_3, R = R′ = Me (**11**); R = C(O)Me, R′ = H (**12**)] and [Pd{η-C_9H_4Bn-1-R-2-R′-3}(N−N)]TfO [R = R′ = H, N−N = bpy (**13a**), tmeda (**13b**); R = R′ = Me, N−N = bpy (**14a**), tmeda (**14b**); R = R′ = Et, N−N = bpy (**15a**), tmeda (**15b**); R = R′ = Ph, N−N = bpy (**16a**), tmeda (**16b**); R = Ph, R′ = H and R = H, R′ = Ph, N−N = bpy (**17a**); R = H, R′ = Ph, N−N = tmeda (**17b**); R = Ph, R′ = Me, N−N = bpy (**18a**), N−N = tmeda (**18b**)]. Complex **3b** reacts with $Me_2C{=}C{=}CH_2$, CS_2, or MeN=C=S to give [Pd(η^3-CMe_2C{C_6H(*E*-CH=CHPh)-6-$(OMe)_3$-2,3,4}CH_2)(tmeda)]Tf O (**19**), [Pd(S_2C{C_6H-(*E*-CH=CHPh)-6-$(OMe)_3$-2,3,4})(tmeda)]TfO (**20**), or [Pd(SC(NMe){C_6H(*E*-CH=CHPh)-6-$(OMe)_3$-2,3,4})(tmeda)]TfO (**21**). The crystal structures of **12**, **17b**, and **18a** have been determined; the hapticities of the indenyl five-membered rings are intermediate betwen η^3 and η^5.

Introduction

Very few (*o*-alkenylaryl)palladium complexes have been reported.[1,2] They could be of interest in the fields of nonlinear optics[3] or organometallic polymers.[4] In this paper we report the synthesis of (*o*-alkenylaryl)palladium complexes through two different ways: (i) reactions of (*o*-formylaryl)palladium complexes with phosphorus ylides (i.e., via a Wittig reaction); (ii) oxidative addition reactions. While the Wittig reaction is a very well-known synthetic method to prepare organic alkenes from carbonyl compounds,[5] only a few examples are known of its application on a coordinated ligand.[3,4] We report here the first syntheses of alkenylaryl complexes through Wittig reactions and discuss their stereoselectivity. When (*o*-acetylaryl)palladium complexes were reacted with a phosphorus ylide, not the expected (*o*-alkenylaryl)palladium complexes but the products of cyclopalladation were obtained. As far as we are aware, these are the only examples of isolated and characterized 3-palladaindan-1-ones.[6] Some of these results have been previously communicated.[7]

Many papers have reported reactions of arylpalladium complexes with alkynes to give a great number of mono-,

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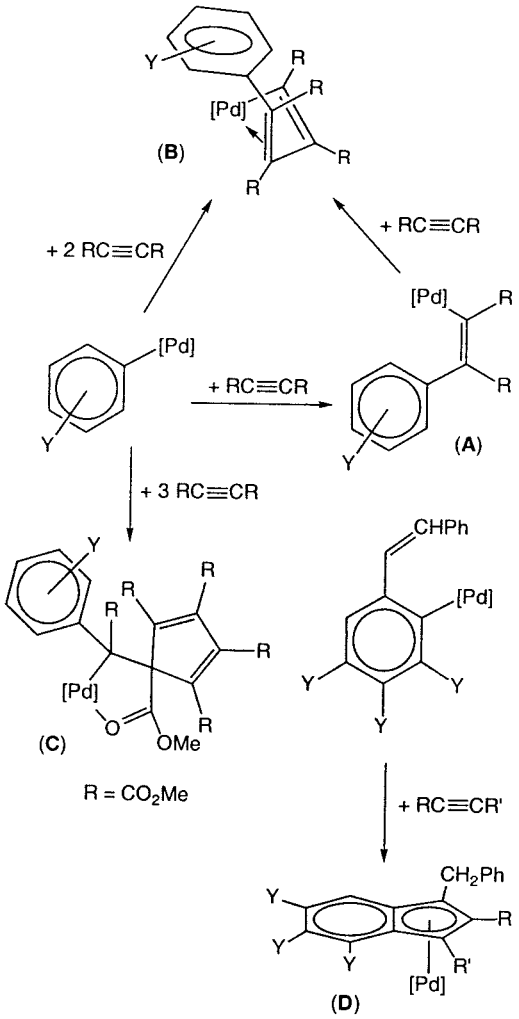
di- and triinserted derivatives most of which are of types **A**−**C**, shown in Scheme 1.[8−18] After depalladation, some of these complexes lead to interesting organic compounds.[9,13,14,19−38] However, despite the great number of studies devoted to this topic, the results we report here have only the precedent of our recent work in which we showed that (2,3,4-trimethoxy-6-alkenylaryl)-palladium complexes reacted with different alkynes to give four indenylpalladium complexes (**D** in Scheme 1).[39] In this paper, we show this type of reaction to be more general as it applies to other arylpalladium complexes−with or without the three methoxy groups−and using the same or other alkynes. Therefore, this represents a new method for the synthesis of indenylpalladium complexes (some highly functionalized) of which very few examples are known.[40−43] In addition, while in most previous studies only symmetrical alkynes were used, we now present the results of using some unsymmetrical ones, which allows us to propose a new empirical scale to predict the regioselectivity of the insertion reactions.

Scheme 1



Finally, we also report reactions of an (*o*-alkenylaryl)-palladium complex with cumulenes X=C=Y leading to π-allyl (X = CH_2, Y = CMe_2), dithiobenzoato (X = Y = S), or *N*-methylthiobenzamidinato (X = S, Y = NMe) complexes. While the insertion of allenes into the Pd−C bond is a well-established method to prepare π-allyl complexes, we are only aware of one example of insertion of CS_2 into a Pd−C bond−that starting from [PdI(Me)(PMe_3)$_2$] giving a dithioacetate complex[44,45] and none for MeN=C=S.

Experimental Section

All reactions involving air- and/or water-sensitive compounds were performed under nitrogen. The following compounds "Pd(dba)$_2$" ([Pd_2(dba)$_3$]·dba),[46,47] [Pd{C_6H(CHO)-6-

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$(OMe)_3$-2,3,4}Cl(bpy)] (**1a**),[48] [Pd(κ^2-{C_6H(C(O)Me)-6-$(OMe)_3$-2,3,4})(μ-Cl)]$_2$,[49] [Pd{C_6H_4(CHO)-2}Br(bpy)] (**2a**), [Pd{C_6H_4-(CHO)-2}Br(tmeda)] (**2b**), and [Pd{C_6H_4(C(O)Me)-2}Br(bpy)] (**8**)[2] were prepared as reported in the literature. Because the hapticity of the indenyl ligand in complexes **11**−**18** is intermediate between η^3 and η^5, we have formulated this ligand as η-indenyl. ($BnPPh_3$)Cl (Bn = benzyl) and 2-bromobenzaldehyde were purchased from Fluka.

Synthesis of 2-Bromostilbene (*E* and *Z* Isomeric Mixture). A commercial 1.6 M diethyl ether solution of MeLi (7.9 cm^3, 12.65 mmol) was added to a suspension of ($BnPPh_3$)Cl (4.92 g, 12.65 mmol) in freshly distilled tetrahydrofuran (45 cm^3) under nitrogen. The mixture was stirred for 10 min. Then 2-bromobenzaldehyde (1.3 cm^3, 11 mmol) was added and the resulting mixture stirred for 20 h under nitrogen. Solvents were evaporated in vacuo, and water (15 cm^3) and pentane (40 cm^3) were added. The organic layer was stirred for 1 h with a large excess of NaBr and then dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness leaving an oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.7−7.0 (several m, aromatics and olefinic protons of the *E* isomer), 6.65 (q, *Z*-CH=CH−).

Synthesis of [Pd{C_6H(CHO)-6-$(OMe)_3$-2,3,4}Cl(tmeda)] (1b). $PdCl_2$ (304 mg, 1.71 mmol) and KCl (300 mg, 4.02 mmol) were dissolved in water (30 mL). [{C_6H(CHO)-6-$(OMe)_3$-2,3,4}$_2$Hg] (1012 mg, 1.71 mmol) and acetone (90 cm^3) were added to the aqueous solution, and the resulting mixture was stirred at room temperature for 2 h. The acetone was evaporated, and further water (80 cm^3) added. The mercurial [Hg-{C_6H(CHO)-6-$(OMe)_3$-2,3,4}Cl] precipitated quantitatively and was filtered off. The resulting yellow solution was treated with a solution of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (200 mg, 1.71 mmol) in dichloromethane (60 cm^3). The organic layer was decanted, and the aqueous solution was extracted with dichloromethane (40 cm^3). The combined extracts were dried with anhydrous $MgSO_4$ and filtered. The solution was concentrated (4 cm^3) and diethyl ether added to precipitate **1b**. Yield: 683 mg, 88%. Mp: 185−186 °C (dec). Λ_M (acetone): 0 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(CO), 1670. ^{1}H NMR (270 MHz, $CDCl_3$, ppm): 11.15 (s, 1 H, CHO), 7.19 (s, 1 H, aryl-H), 4.22, 3.95 and 3.83 (s 3 H, MeO), 2.55−2.80 (m, 4 H, CH_2CH_2), 2.73, 2.68, 2.54, and 2.29 (s, 3 H, MeN). ^{13}C NMR (68 MHz, $CDCl_3$, ppm): 195.89 (CHO), 155.53, 151.15, 146.49, 143.32, and 136.36 (C-aryl), 106.52 (CH-aryl), 63.15, 61.02, 60.90, 58.74, and 55.90 (MeO and CH_2CH_2), 52.10, 51.07, 48.32, and 47.96 (MeN). Anal. Calcd for $C_{16}H_{27}ClN_2O_4Pd$: C, 42.40; H, 6.00; N, 6.18. Found: C, 42.17; H, 5.99; N, 6.18.

Synthesis of [Pd{C_6H(CH=CHPh)-6-$(OMe)_3$-2,3,4}Cl(bpy)] (3a). A 1.6 M solution of ^{n}BuLi in hexane (0.38 cm^3, 0.61 mmol) was added to a suspension of benzyltriphenylphosphonium chloride (237 mg, 0.61 mmol) in diethyl ether (8 cm^3) and stirred for 30 min under nitrogen. **1a** (200 mg, 0.41 mmol) was added to give a yellow suspension, which was stirred for 20 h. The mixture was filtered, and the solid residue was washed with diethyl ether (4 × 10 cm^3), benzene/diethyl ether (1:1, 2 × 5 cm^3), diethyl ether (2 × 10 cm^3), and water (3 × 10 cm^3) and then dissolved in dichloromethane and stirred with anhydrous $MgSO_4$. The suspension was filtered over anhydrous $MgSO_4$ and the clear solution concentrated to 1 cm^3. Diethyl ether was added to precipitate yellow **3a** as a *Z*/*E* mixture (1:3). Yield: 191 mg, 83%. The pure *E*-compound can be isolated by crystallization from chloroform/diethyl ether. Yield: 32 mg, 14%. Mp: 188−190 °C (dec). Λ_M (acetone): 0 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 9.30−9.33 (m, 1 H, bpy), 8.36 (d, 1 H, C*H*=CH, ^3J = 16 Hz), 7.83−8.05, 7.70−7.72, 7.45−7.60, 7.05−7.27 (m, 12 H, bpy and C_6H_5), 6.96 (s, 1 H, aryl-H), 6.94 (d, 1 H, CH=C*H*, ^3J = 16 Hz), 4.11, 3.93 and 3.91 (s, 3 H, MeO), 1.64 (s, H_2O, 2 H). ^{13}C NMR (68 MHz, $CDCl_3$, ppm): 156.20, 154.51, 153.63, 151.69, 151.19, 149.37, 141.68, 139.08, 138.46, 136.87, 134.07, 128.39, 126.66, 126.60, 126.43, 125.44, 122.16, and 121.42 (aromatic CH and C), 104.73 (Aryl-*C*H), 61.06, 61.01, and 56.22 (MeO). Anal. Calcd for $C_{27}H_{25}ClN_2O_3Pd\cdot H_2O$: C, 55.40; H, 4.65; N, 4.79. Found: C, 55.66; H, 4.42; N, 4.80.

Synthesis of [Pd{C_6H(*E*-CH=CHPh)-6-$(OMe)_3$-2,3,4}Cl(tmeda)] (3b). Benzyltriphenylphosphonium chloride (643 mg, 1.66 mmol), potassium *tert*-butoxide (186 mg, 1.66 mmol), and **1b** (500 mg, 1.10 mmol) were reacted for 20 h in dry dichloromethane. The mixture was evaporated to dryness and the residue stirred in diethyl ether for 1 h. The suspension was filtered, and the solid was washed with diethyl ether (4 × 10 cm^3), benzene/diethyl ether (1:1, 2 × 5 cm^3), diethyl ether (2 × 10 cm^3), and water (3 × 10 cm^3) and then dissolved in dichloromethane and stirred with anhydrous $MgSO_4$. The suspension was filtered over anhydrous $MgSO_4$ and the clear solution concentrated to 1 cm^3. Diethyl ether was added to precipitate yellow **3b**. Yield: 450 mg, 77%. Mp: 196−197 °C (dec). Λ_M (acetone): 0 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 8.50 (d, 1 H, C*H*=CH, ^3J = 16 Hz), 7.55−7.65, 7.10−7.40 (m, 5 H, C_6H_5), 7.04 (d, 1 H, CH=C*H*, ^3J = 16 Hz), 6.84 (s, 1 H, aryl-H), 4.27, 3.89, and 3.86 (s, 3 H, MeO), 2.50−2.75 (m, 4 H, CH_2CH_2), 2.72 (s, 6 H, 2 × MeN), 2.52 and 2.25 (s, 3 H, MeN). ^{13}C NMR (68 MHz, $CDCl_3$, ppm): 154.73, 150.50, 141.04, 138.53, 136.79, and 131.73 (aromatic C), 128.52 and 126.00 (*o*,*m*-C_6H_5), 134.12, 126.52, and 125.18 (H*C*=*C*H and *p*-CHC_6H_5), 104.69 (CH aryl), 62.80 (CH_2), 60.94 and 60.85 (MeO), 58.34 (CH_2), 55.95 (MeO), 51.59, 50.63, 47.95, and 47.57 (MeN). Anal. Calcd for $C_{23}H_{33}ClN_2O_3Pd$: C, 52.38; H, 6.31; N, 5.31. Found: C, 52.29; H, 6.61; N, 5.40. Single crystals of **3b** were obtained by liquid diffusion of diethyl ether into a solution of **3b** in chloroform.

Synthesis of [Pd{C_6H(CH=CHpy)-6-$(OMe)_3$-2,3,4}Cl(bpy)] (4). Yellow **4** was prepared analogously to **3a** from ((2-pyridyl)methyl)triphenylphosphonium chloride (237 mg, 0.61 mmol), a 1.6 M solution of ^{n}BuLi in hexane (0.38 cm^3, 0.61 mmol), and **1a** (200 mg, 0.41 mmol) to form a *Z*/*E* mixture (1:4). Yield: 183 mg, 79%. The pure *E*-compound can be isolated by crystallization from dichloromethane/diethyl ether. Yield: 46 mg, 19%. Mp: 167−169 °C (dec). Λ_M (acetone): 11 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 9.27−9.31 (m, 1 H, bpy), 8.67 (d, 1 H, C*H*=CH, ^3J = 16 Hz), 8.40−8.46, 7.46−8.15, 6.95−7.28 (m, 11 H, bpy and py), 7.13 (d, 1 H, CH=C*H*, ^3J = 16 Hz), 7.06 (s, 1 H, aryl-H), 5.30 (s, 1 H, CH_2Cl_2), 4.10, 3.95, and 3.91 (s, 3 H, MeO). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 157.16, 156.24, 154.55, 153.71, 151.74, 151.29, 149.39, 149.23, 142.20, 139.19, 138.58, 138.00, 136.26, 136.17, 126.77, 126.47, 125.85, 122.32, 121.50, 121.15, and 120.95 (aromatic CH and C), 105.16 (Aryl*C*H), 61.17, 61.08, and 56.04 (MeO), 53.8 (CH_2Cl_2). Anal. Calcd for $C_{26}H_{24}ClN_3O_3Pd\cdot 0.5\ CH_2Cl_2$: C, 52.11; H, 4.13; N, 6.88. Found: C, 52.05; H, 4.31; N, 6.65.

Synthesis of [Pd{C_6H(*E*-CH=CHCl)-6-$(OMe)_3$-2,3,4}Cl(tmeda)] (5). Pale yellow **5** was prepared analogously to **3b** from (chloromethyl)triphenylphosphonium chloride (527 mg, 1.52 mmol), potassium *tert*-butoxide (170 mg, 1.52 mmol), and **1b** (500 mg, 1.10 mmol). Yield: 433 mg, 81%. Mp: >350 °C. Λ_M (acetone): 0 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.91 (d, 1 H, C*H*=CH, ^3J = 13.5 Hz), 6.84 (d 1 H, CH=C*H*, ^3J = 13.5 Hz), 6.53 (s, 1 H, aryl-H), 4.20, 3.87, and 3.79 (s, 3 H, MeO), 2.55−2.75 (m, 4 H, CH_2CH_2), 2.69 (s, 6 H, 2 × MeN), 2.51 and 2.32 (s, 6 H, MeN). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 154.82, 150.40, and 141.33 (C-aryl), 137.55 (H*C*=CH), 134.39 and 130.62 (C-aryl), 115.17 (HC=*C*H), 105.39 (aryl-*C*H), 62.83 (CH_2), 60.70 (2 × MeO), 58.36 (CH_2), 55.93 (MeO), 51.40, 50.76, 47.79 and 47.73 (MeN). Anal. Calcd for $C_{17}H_{28}Cl_2N_2O_3Pd$: C, 42.04; H, 5.81; N, 5.77. Found: C, 42.32; H, 5.86; N, 5.57.

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Synthesis of [Pd{C_6H_4(CH=CHPh)-2}Br(bpy)] (6a). Method A. A 1.6 M solution of ^{n}BuLi in hexane (0.32 cm^3, 0.51 mmol) was added to a suspension of benzyltriphenylphosphonium chloride (198 mg, 0.51 mmol) in tetrahydrofuran (15 cm^3) under nitrogen, and the resulting mixture was stirred for 10 min. Complex **2a** (200 mg, 0.44 mmol) was added and the mixture stirred for a further 20 h. The solvent was removed in vacuo and the residue washed with diethyl ether (4 × 5 cm^3) and water (2 × 15 cm^3) and then redissolved in dichloromethane; an excess of NaBr was added to the solution, which was stirred for 1 h. The resulting suspension was treated with anhydrous magnesium sulfate and filtered. From the filtrate, evaporation of the solvent and addition of diethyl ether precipitated yellow **6a** as an *E*/*Z* mixture (2.6:1). Yield: 124 mg, 54%.

Method B. 2-Bromostilbene (*E* and *Z* mixture) (543 mg, 2.1 mmol) was added to "Pd(dba)$_2$" (400 mg, 0.68 mmol) and bpy (110 mg, 0.68 mmol), and the resulting suspension was slowly heated to 100 °C, until the mixture became brown (1 h). The solvent was removed in vacuo, the residue was extracted with dichloromethane (4 × 10 cm^3), and the extracts were filtered over anhydrous magnesium sulfate. The resulting solution was evaporated to dryness and the residue triturated with diethyl ether to give complex **6a** as an *E*/*Z* mixture (1:1.7). Yield: 249 mg, 68%. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 9.39−9.46 (m, bpy), 8.22 (d, −C*H*=CHPh *E*, $^3J_{HH}$ = 16 Hz), 7.37 (d, −C*H*=CHPh *Z*, $^3J_{HH}$ = 12 Hz), 6.74−8.04 (several m, aromatic H's) 6.40 (d, −CH=C*H*Ph *Z*, $^3J_{HH}$ = 12 Hz). Anal. Calcd for $C_{24}H_{19}BrN_2Pd$: C, 55.29; H, 3.67; N, 5.37. Found: C, 55.48; H, 3.55; N, 5.10.

Synthesis of [Pd{C_6H_4(CH=CHPh)-2}Br(tmeda)] (6b). Yellow complex **6b** was similarly prepared (method A) from ^{n}BuLi (0.34 cm^3, 0.55 mmol), benzyltriphenylphosphonium chloride (214 mg, 0.55 mmol), and **2b** (200 mg, 0.48 mmol) as a 9:1 *E*/*Z* mixture. Yield: 203 mg, 87%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 8.38 (d, −C*H*=CHPh *E*, $^3J_{HH}$ = 16 Hz), 6.64−7.65 (several m, aromatic H's), 7.28 (d, −CH=C*H*Ph *E*, $^3J_{HH}$ = 16 Hz), 6.52 (d, −CH=C*H*Ph *Z*, $^3J_{HH}$ = 12 Hz), 2.39−2.81 (m, CH_2), 2.81 (s, Me, *Z*), 2.72 (s, Me, *E*), 2.68 (s, Me, *E*), 2.65 (s, Me, *Z*), 2.58 (s, Me, *Z*), 2.47 (s, Me, *E*), 2.39 (s, Me, *Z*), 2.15 (s, Me, *E*). Anal. Calcd for $C_{20}H_{27}BrN_2Pd$: C, 49.86; H, 5.65; N, 5.81. Found: C, 49.87; H, 5.45; N, 5.98.

Synthesis of [Pd{C_6H(C(O)Me)-6-$(OMe)_3$-2,3,4}Cl(tmeda)] (7). A solution of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (520 mg, 4.47 mmol) in dichloromethane (20 cm^3) was added to a suspension of [Pd(κ^2-{C_6H(C(O)Me)-6-$(OMe)_3$-2,3,4})(μ-Cl)]$_2$ (1440 mg, 2.05 mmol) in dichloromethane (30 cm^3). After 30 min of stirring, the resulting solution was passed through Celite and evaporated to 2 cm^3. The yellow compound **7** precipitated by addition of diethyl ether. Yield: 1752 mg, 91%. Mp: 143−145 °C (dec). Λ_M (acetone): 0 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(CO), 1650. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 7.05 (s, 1 H, aryl-H), 4.23, 3.93, and 3.83 (s, 3 H, MeO), 2.45−3.00 (m, 4 H, CH_2CH_2), 2.90, 2.75, 2.66, 2.61, and 2.26 [s, 3 H, MeN and C(O)Me]. ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 201.33 [*C*(O)Me], 154.85, 149.43, 144.55, 139.23, and 135.80 (C-aryl), 110.11 (CH-aryl), 62.70 (CH_2), 60.54 (OMe), 60.44 (OMe), 58.56 (CH_2), 55.99 (MeO), 51.38, 50.68, 48.47, and 47.79 (MeN), 29.68 [C(O)*C*H$_3$]. Anal. Calcd for $C_{17}H_{29}ClN_2O_4Pd$: C, 43.69; H, 6.26; N, 5.99. Found: C, 43.47; H, 6.44; N, 5.94.

Synthesis of [Pd(κ^2-{C_6H(C(O)CH_2)-6-$(OMe)_3$-2,3,4})(tmeda)] (9). NaOMe (1.5 mmol of a freshly titrated solution in methanol) was added to a solution of **7** (600 mg, 1.29 mmol) in methanol (5 cm^3). The mixture was stirred for 5 min and evaporated to dryness in vacuo, and the residue was stirred with dichloromethane (5 cm^3) and anhydrous $MgSO_4$. The suspension was filtered over anhydrous $MgSO_4$ and concentrated to 1 cm^3, and the yellow complex **9** was precipitated by addition of diethyl ether. Yield: 472 mg, 87%. Mp: 157−158 °C (dec). Λ_M (acetone): 0 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(CO), 1642. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 6.97 (s, 1 H, aryl-H), 3.94, 3.88, and 3.82 (s, 3 H, MeO), 2.55−2.80 (m, 4 H, CH_2-CH_2), 2.74 (s, 6 H, NMe_2), 2.67 [s, 2 H, C(O)CH_2], 2.59 (s, 6 H, NMe_2). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 203.97 [*C*(O)CH_2], 158.57, 150.50, 144.47, 142.26, and 138.98 (C-aryl), 103.31 (CH-aryl), 61.51 (CH_2), 61.23 (OMe), 60.58 (OMe), 59.96 (CH_2), 55.66 (MeO), 49.32 and 49.19 (Me_2N), 41.98 [C(O)*C*H$_2$]. Anal. Calcd for $C_{17}H_{28}N_2O_4Pd$: C, 47.39; H, 6.55; N, 6.50. Found: C, 47.30; H, 6.75; N, 6.38. Single crystals of **9** were obtained by liquid diffusion of diethyl ether or hexane into a solution of **9** in dichloromethane.

Synthesis of [Pd(κ^2-{C_6H_4(C(O)CH_2)-2})(bpy)] (10). Complex **8** (80 mg, 0.18 mmol) in methanol (5 cm^3) was treated with a solution of NaOMe in methanol (0.3 cm^3, 0.26 mmol) for 20 h. The solvent was removed in vacuo and the residue redissolved in dichloromethane (15 cm^3). Anhydrous magnesium sulfate was added and the mixture stirred for 15 min. The suspension was filtered, the resulting solution evaporated, and diethyl ether added to precipitate **10** as a yellow solid. Yield: 53 mg, 79%. Mp: 155 °C (dec). IR (cm^{-1}): ν(CO), 1644. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 8.85−8.87 (m, 1 H, bpy), 8.53−8.55 (m, 1 H, bpy), 8.12−8.16 (m, 2 H, bpy), 7.93−8.02 (m, 2 H, bpy), 7.73 (b d, 1 H, H3 or H6, $^3J_{HH}$ = 7 Hz), 7.55−7.58 (m, 1 H, H6 or H3), 7.47−7.52 (m, 1 H, bpy), 7.41−7.46 (m, 1 H, bpy), 7.13−7.24 (m, 2 H, H4 and H5), 3.17 (s, 2 H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 207.83 (CO), 155.84, 154.78, 150.77, and 149.89 (CH), 148.70, 138.44, 132.75, 128.68, 126.07, 125.87, 124.02, 123.86, 122.55, and 122.26 (CH), 44.39 (CH_2). Anal. Calcd for $C_{18}H_{14}N_2OPd$: C, 56.79; H, 3.71; N, 7.36. Found: C, 56.49; H, 3.68; N, 7.48.

Synthesis of [Pd{η -C_9HBn-1-Me_2-2,3-$(OMe)_3$-5,6,7}(tmeda)]TfO (11). 2-Butyne (30 mg, 0.56 mmol) was added to a suspension of **3b** (100 mg, 0.19 mmol) and Tl(TfO) (67 mg, 0.19 mmol; TfO = CF_3SO_3) in CH_2Cl_2 (5 cm^3). The mixture was stirred for 20 h and filtered over anhydrous $MgSO_4$. The solution was concentrated to 1 cm^3, and diethyl ether was added to precipitate **11** as a red-violet solid. Yield: 101 mg, 77%. Mp: 137−139 °C. Λ_M (acetone): 118 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 7.15−7.40 (m, C_6H_5, 5 H), 6.28 (s, 1 H, Aryl CH), 3.88, 3.80, and 3.77 (s, 3 H, MeO), 3.40 and 3.26 (AB system, 2 H, C*H*$_2$Ph, $^2J_{HH}$ = 15 Hz), 2.60−2.95 (m, 4 H, CH_2CH_2), 2.75, 2.68, 2.67 and 2.63 (s, 3 H, MeN), 2.31, 1.58 (s, indenyl-CH_3, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 153.55, 145.33, 141.45, 135.18, and 133.46 (C-aryl), 128.68 and 128.02 (*o*, *m*-C_6H_5), 126.75 (*p*-C_6H_5), 124.32 (indenyl-C), 122.32 (C-aryl), 96.16 (Aryl-*C*H), 88.47 and 88.01 (indenyl-C), 61.16 (*C*H$_2$*C*H$_2$), 60.91 (2 × MeO), 56.41 (MeO), 51.40, 51.26, 51.17, and 50.94 (MeN), 30.76 (Ph*C*H$_2$), 12.17 (indenyl-*C*H$_3$). Anal. Calcd for $C_{28}H_{39}F_3N_2O_6PdS$: C, 48.38; H, 5.66; N, 4.03. Found: C, 48.01; H, 5.88; N, 4.07.

Synthesis of [Pd{η -C_9H_2Bn-1-(Ac)-2-$(OMe)_3$-5,6,7}(tmeda)]TfO (12). Crude **12** was similarly prepared from 3-butyne-2-one (35 mg, 0.51 mmol), **3b** (120 mg, 0.23 mmol), and Tl(TfO) (81 mg, 0.23 mmol). The compound was purified by chromatography: Elution with chloroform−acetone (1:1) rendered dark red **12**. Yield: 52 mg, 32%. Mp: 236−237 °C. Λ_M (acetone): 118 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.20−7.31 (m, 5 H, C_6H_5), 6.54 (s, 1 H, aryl-H or indenyl-CH), 6.18 (s, 1 H, indenyl-CH or aryl-H), 4.23 (d, 1 H, C*H*$_2$Ph, $^2J_{HH}$ = 14 Hz), 4.03, 3.87, and 3.84 (s, 3 H, MeO), 3.38 (d, 1 H, C*H*$_2$Ph, $^2J_{HH}$ = 14 Hz), 2.50−3.15 (m, 4 H, CH_2CH_2), 2.96, 2.85, 2.73, and 2.67 (s, 3 H, MeN), 2.48 [s, 3 H, C(O)CH_3]. ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 190.62 (C=O), 156.55, 145.52, 142.92, 135.81, and 133.42 (C-aryl), 128.68 and 128.33 (*o*,*m*-C_6H_5), 126.89 (*p*-C_6H_5), 120.43 and 118.08 (C-aryl and indenyl-C), 96.68 (R-*C*H), 94.23 (indenyl-C), 76.44 (indenyl-CH), 62.00 (*C*H$_2$*C*H$_2$), 61.38 and 61.23 (MeO), 61.09 (CH_2*C*H$_2$), 56.54 (MeO), 54.61, 53.04, 51.81, and 51.36 (MeN), 31.04 (Ph*C*H$_2$), 27.79 [C(O)*C*H$_3$]. Anal. Calcd for $C_{28}H_{37}F_3N_2O_7PdS$: C, 47.43; H, 5.26; N, 3.95; S, 4.52. Found: C, 47.64; H, 5.30; N, 4.02; S, 4.49. Single crystals of **12** were obtained by liquid diffusion of diethyl ether into a solution of **12** in chloroform.

Synthesis of [Pd(η-C_9H_6Bn-1)(bpy)]TfO (13a). A saturated dichloromethane solution of HC≡CH (10 cm^3) was added to a suspension of **6a** (60 mg, 0.11 mmol) and Tl(TfO) (41 mg, 0.11 mmol) in dichloromethane (10 cm^3). The mixture was stirred at room temperature for 20 h and then filtered over Celite giving a red solution, which was concentrated to 1 cm^3. Diethyl ether was added to precipitate **13a** as a brown solid. Yield: 56 mg, 83%. Mp: 140 °C. Λ_M (acetone): 120 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 8.00−8.94 (several m, 8 H, bpy), 6.98−7.79 (several m, 9 H aromatic H's), 6.84 (d, 1 H, H2 or H3, $^3J_{HH}$ = 3 Hz), 6.30 (d, 1 H, H3 or H2, $^3J_{HH}$ = 3 Hz), 3.63 and 3.48 (AB system, 2 H, CH_2Ph, $^2J_{HH}$ = 15 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 156.67 (CH bpy), 153.69 (C bpy), 152.56 (CH bpy), 152.03 (C bpy), 141.27 and 140.77 (CH bpy), 136.97, 136.87, and 135.47 (C), 129.02, 128.51, 128.20, 127.75, 127.42, 127.37, 124.39, 124.12, 118.97, 117.01, and 112.57 (CH), 96.55 (C), 80.49 (CH), 32.77 (CH_2). HR FAB MS: calcd for $C_{26}H_{21}N_2Pd$, *m/e* 465.0745 (32.4), 466.0755 (74.4), 467.0739 (100), 469.0744 (80.4), 471.0756 (37.3); found, *m/e* 465.0733 (30.3), 466.0738 (73.2), 467.0734 (100), 469.0741 (75.8), 471.0753 (37.8).

Synthesis of [Pd(η-C_9H_6Bn-1)(tmeda)]TfO (13b). The reddish brown complex **13b** was similarly prepared from **6b** (60 mg, 0.12 mmol) and Tl(TfO) (44 mg, 0.12 mmol). Yield: 38 mg, 53%. Mp: 130 °C. Λ_M (acetone): 141 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 6.96−7.32 (several m, 9 H aromatic H's), 6.90 (d, 1 H, H2 or H3, $^3J_{HH}$ = 3 Hz), 5.64 (d, 1 H, H3 or H2, $^3J_{HH}$ = 3 Hz), 3.31 and 3.24 (AB system, 2 H, CH_2Ph, $^2J_{HH}$ = 15 Hz), 2.59−2.89 (m, 4 H, CH_2CH_2), 2.89 (s, 3 H, Me), 2.79 (s, 3 H, Me), 2.70 (s, 3 H, Me), 2.59 (s, 3 H, Me). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 136.66, 136.46 and 135.89 (C), 128.90, 128.18, 127.64, 127.52, 127.12, 117.41, 115.92, and 112.32 (CH), 94.19 (C), 77.59 (CH), 61.78 and 60.86 (NCH_2), 53.94, 53.13, 51.87, and 51.73 (Me), 32.91 (CH_2Ph). Anal. Calcd for $C_{23}H_{29}F_3N_2O_3PdS$: C, 47.88; H, 5.07; N, 4.86; S, 5.56. Found: C, 47.82; H, 5.26; N, 4.90; S, 5.70.

Synthesis of [Pd(η-C_9H_4Bn-1-Me_2-2,3)(bpy)]TfO (14a). The brown complex **14a** was similarly prepared from **6a** (60 mg, 0.11 mmol), Tl(TfO) (41 mg, 0.11 mmol), and MeC≡CMe (0.017 cm^3, 0.22 mmol). Yield: 52 mg, 73%. Mp: 132 °C. Λ_M (acetone): 123 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 6.94−8.52 (several m, 17 H aromatic H's), 3.98 and 3.50 (AB system, 2 H, CH_2Ph, $^2J_{HH}$ = 15 Hz), 2.41 and 1.73 (s, 3 H, Me). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 153.01 (C bpy), 152.35 (CH bpy), 151.44 (C bpy), 141.13 (CH bpy), 137.26, 136.58, and 134.73 (C), 128.94, 128.26, 127.95, 127.73, 127.53, and 127.11 (CH), 126.53 (C), 124.42, 116.10, and 115.80 (CH), 91.46 and 91.42 (C), 31.09 (CH_2Ph), 12.72 and 10.48 (Me). Anal. Calcd for $C_{29}H_{25}F_3N_2O_3PdS$: C, 54.00; H, 3.91; N, 4.34; S, 4.97. Found: C, 53.29; H, 3.93; N, 4.37; S, 5.05. HR FAB MS: calcd for $C_{28}H_{25}N_2Pd$, *m/e* 493.1058 (31.9), 494.1068 (73.9), 495.1052 (100), 497.1057 (79.7), 499.1069 (37.2); found, *m/e* 493.1073 (35.4), 494.1086 (69.0), 495.1078 (100), 497.1075 (83.6), 499.1082 (35.9)

Synthesis of [Pd(η-C_9H_4Bn-1-Me_2-2,3)(tmeda)]TfO (14b). The reddish-brown complex **14b** was similarly prepared from **6b** (60 mg, 0.12 mmol), Tl(TfO) (44 mg, 0.12 mmol), and MeC≡CMe (0.018 cm^3, 0.24 mmol). Yield: 42 mg, 56%. Mp: 115 °C. Λ_M (acetone): 110 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 6.80−7.28 (several m, 9 H aromatic H's), 3.48 and 3.34 (AB system, 2 H, CH_2Ph, $^2J_{HH}$ = 15 Hz), 2.5−3.0 (m, 4 H, CH_2-CH_2), 2.79, 2,69, 2.59, and 2.52 (s, 3 H, MeN), 2.40 and 1.47 (s, 3 H, Me). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 137.19, 136.35, and 134.93 (C), 128.85, 128.06, 127.17, 126.99, and 126.90 (CH), 126.36 (C), 114.83 and 114.47 (CH), 88.82 and 88.73 (C), 61.07 (2 C, CH_2CH_2), 51.82, 51.58, 51.36, and 51.10 (MeN), 31.97 (CH_2Ph), 12.40 and 10.21 (Me). HR FAB MS: calcd for $C_{24}H_{33}N_2Pd$, *m/e* 453.1684 (32.9), 454.1694 (74.9), 455.1678 (100), 457.1683 (81.1), 459.1695 (37.4); found, *m/e* 453.1679 (36.0), 454.1694 (69.4), 455.1696 (100), 457.1691 (80.0), 459.1689 (38.6).

Synthesis of [Pd(η-C_9H_4Bn-1-Et_2-2,3)(bpy)]TfO (15a). The orange brown complex **15a** was similarly prepared from **6a** (60 mg, 0.11 mmol), Tl(TfO) (41 mg, 0.11 mmol), and EtC≡CEt (0.025 cm^3, 0.22 mmol). Yield: 49 mg, 66%. Mp: 127 °C. Λ_M (acetone): 103 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 6.95−8.57 (several m, 17 H aromatic H's), 3.92 and 3.42 (AB system, 2 H, CH_2Ph, $^2J_{HH}$ = 15 Hz), 2.19−2.61 (m, 4 H, 2 × C$H_2$$CH_3$), 1.41 and 0.89 (t, 3 H, Me, $^3J_{HH}$ = 7 Hz). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 153.16 (C bpy), 151.94 (CH bpy), 151.65 (C bpy), 141.26 (CH bpy), 136.92, 135.61, 135.10, and 131.52 (C), 128.99, 128.13, 128.01, 127.76, 127.52, 127.36, 127.18, 124.70, 116.27, and 116.20 (CH), 96.58 and 91.60 (C), 31.05 (*C*H_2Ph), 19.36 and 18.92 (*C*H_2Me), 16.42 and 11.58 (Me). Anal. Calcd for $C_{31}H_{29}F_3N_2O_3PdS$: C, 55.32; H, 4.34; N, 4.16; S, 4.76. Found: C, 55.08; H, 4.18; N, 4.19; S, 4.53.

Synthesis of [Pd(η-C_9H_4Bn-1-Et_2-2,3)(tmeda)]TfO (15b). The reddish brown complex was obtained from **6b** (60 mg, 0.12 mmol), Tl(TfO) (44 mg, 0.12 mmol), and EtC≡CEt (0.027 cm^3, 0.24 mmol). It was obtained as a reddish brown oil. Yield: 41 mg, 54%. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 6.78−7.32 (several m, 9 H aromatic H's), 3.51 and 3.32 (AB system, 2 H, CH_2Ph, $^2J_{HH}$ = 15 Hz), 2.5−3.0 (m, 6 H, CH_2CH_2 + CH_2Me), 2.76, 2.67, 2.58, and 2.52 (s, 3 H, MeN), 2.06−2.17 (m, 2 H CH_2Me), 1.33 and 1.18 (t, 3 H, Me, $^3J_{HH}$ = 7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 136.38, 135.09, 135.07, and 131.94 (C), 128.91, 127.79, 127.34, 127.09, 127.05, 115.26, and 114.90 (CH), 94.12 and 89.43 (C), 61.24 (2 C, CH_2CH_2), 51.96 and 51.70 (MeN), 51.32 (2 × NMe), 30.85 (*C*H_2Ph), 18.71 (2 × *C*H_2Me), 17.45 and 11.70 (Me). HR FAB MS: calcd for $C_{26}H_{37}N_2Pd$, *m/e* 481.1997 (32.3), 482.2007 (74.4), 483.1991 (100), 485.1996 (80.3), 487.2008 (37.3); found, *m/e* 481.2043 (32.5), 482.2063 (78.5), 483.2058 (100), 485.2068 (84.7), 487.2081 (41.0).

Synthesis of [Pd(η-C_9H_4Bn-1-Ph_2-2,3)(bpy)]TfO (16a). The brown complex **16a** was similarly prepared from **6a** (60 mg, 0.11 mmol), Tl(TfO) (41 mg, 0.11 mmol), and PhC≡CPh (39 mg, 0.22 mmol). Yield: 46 mg, 54%. Mp: 180 °C. Λ_M (acetone): 109 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.81−8.79 (several m, 8 H bpy), 6.99−7.55 (several m, 19H, aromatic H's), 3.85 and 3.74 (AB system, 2 H, CH_2Ph, $^2J_{HH}$ = 13 Hz). ^{13}C NMR (75 MHz, CD_2Cl_2): 153.39 (2xC bpy), 152.49, 151.91, 141.40, and 141.06 (CH bpy), 135.15, 134.62, 133.94, and 131.15 (C), 131.05 (CH), 130.49 and 129.85 (C), 129.77, 129.52, 129.16, 129.02, 128.69, 128.61, 128.51, 127.85, 127.75, 127.06, 126.98, 124.42, 123.75, 118.51, and 117.46 (CH), 94.89 and 94.21 (C), 31.05 (CH_2Ph). Anal. Calcd for $C_{39}H_{29}F_3N_2O_3PdS$: C, 60.90; H, 3.80; N, 3.64; S, 4.17. Found: C, 60.90; H, 3.96; N, 3.89; S, 4.05.

Synthesis of [Pd(η-C_9H_4Bn-1-Ph_2-2,3)(tmeda)]TfO (16b). The reddish brown complex **16b** was similarly prepared from **6b** (60 mg, 0.12 mmol), Tl(TfO) (44 mg, 0.12 mmol), and PhC≡CPh (44 mg, 0.24 mmol). Yield: 64 mg, 73%. Mp: 160 °C (dec). Λ_M (acetone): 135 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 6.85−7.47 (several m, 19 H, aromatic H's), 3.40 and 3.33 (AB system, 2 H, CH_2Ph, $^2J_{HH}$ = 14 Hz), 2.5−2.9 (m, 4 H, CH_2CH_2), 3.05, 2.64, 2.50 and 2.05 (s, 3 H, MeN). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 135.40, 134.77, 132.87, 131.47. 130.81 and 130.44 (C), 130.94, 129.09, 128.99, 128.95, 128.75, 128.57, 128.48, 128.41, 127.95, 127.75, 126.81, 117.43, and 116.95 (CH), 91.46 and 93.05 (C), 62.05 and 61.37 (CH_2N), 53.41, 52.04, 51.17, and 49.00 (MeN), 30.89 (CH_2Ph). Anal. Calcd for $C_{35}H_{37}F_3N_2O_3PdS$: C, 57.65; H, 5.11; N, 3.84; S, 4.40. Found: C, 57.44; H, 5.23; N, 4.04; S, 4.30.

Syntheses of [Pd(η-C_9H_5Bn-1-Ph-3)(bpy)]TfO (17a) and [Pd(η-C_9H_5Bn-1-Ph-2)(bpy)]TfO (17a′). The mixture of regioisomers **17a** and **17a′** was similarly prepared from **6a** (60 mg, 0.11 mmol), Tl(TfO) (41 mg, 0.11 mmol), and PhC≡CPh (0.024 cm^3, 0.22 mmol). Color: brown. Yield: 56 mg, 73%. **17a**:**17a′**= 1.5:1. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 7.0−9.0 (several m, aromatic H's), 6.93 (s, H2 indenyl **17a**), 6.43 (s, 1 H, H3 indenyl **17a′**), 3.89 (s, 2 H, CH_2Ph **17a′**), 3.74 and 3.57 (AB system, 2 H, CH_2Ph **17a**, $^2J_{HH}$ = 15 Hz). Anal. Calcd for

$C_{33}H_{25}F_3N_2O_3PdS$: C, 57.19; H, 3.64; N, 4.04; S, 4.63. Found: C, 57.29; H, 3.71; N, 4.13; S, 4.25.

Synthesis of [Pd(η-C_9H_5Bn-1-Ph-3)(tmeda)]TfO (17b). The brown complex **17b** was similarly prepared from **6b** (60 mg, 0.12 mmol), Tl(TfO) (44 mg, 0.12 mmol), and PhC≡CH (0.027 cm^3, 0.24 mmol). Yield: 59 mg, 75%. Mp: 139 °C (dec). Λ_M (acetone): 155 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.05−7.91 (several m, 14 H, aromatic H's), 7.03 (s, 1 H, H2 indenyl), 3.34 (s, 2 H, C*H*$_2$Ph), 2.50−2.80 (m, 4 H, CH_2-CH_2), 2.76, 2.50, 2.14, and 2.05 (s, 3 H, MeN). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 137.41, 135.85, 134.09, and 132.72 (C), 129.74, 129.16, 128.91, 128.70, 128.29, 127.61, 127.38, 127.12, 117.80, and 116.36 (CH), 110.38 (CH2 indenyl), 92.97 and 91.81 (C), 61.50 and 61.12 (CH_2N), 52.28, 51.41, 51.20, and 49.14 (Me), 32.87 (*C*H$_2$Ph). HR FAB MS: calcd for $C_{28}H_{33}N_2$-Pd, *m*/*e* 501.1684 (31.9), 502.1694 (73.9), 503.1678 (100), 505.1683 (79.6), 507.1695 (37.2); found, *m*/*e* 501.1679 (30.4), 502.1695 (75.2), 503.1692 (100), 505.1686 (74.3), 507.1715 (37.2). Single crystals of **17b** were were grown by liquid diffusion of diethyl ether into a solution of **17b** in dichloromethane.

Synthesis of [Pd(η-C_9H_4Bn-1-Ph-2-Me-3)(bpy)]TfO (18a). The brown complex **18a** was similarly prepared from **6a** (100 mg, 0.18 mmol), Tl(TfO) (68 mg, 0.18 mmol), and PhC≡CMe (0.045 cm^3, 0.36 mmol). Yield: 72 mg, 70%. Mp: 154 °C. Λ_M (acetone): 116 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 8.8−7.5 (several m, 8 H bpy), 7.38 (bs, 5 H, Ph-2 indenyl), 7.2−7.0 (several m, 9H, aromatic H's), 3.78 and 3.53 (AB system, 2 H, C*H*$_2$Ph, $^2J_{HH}$ = 14 Hz), 1.68 (s, 3 H, Me). ^{13}C NMR (50 MHz, CD_2Cl_2, ppm): 153.23 and 153.20 (C bpy), 152.46, 151.43, 141.17, and 141.08 (CH bpy), 136.77, 135.60, 135.01, 131.31, and 130.75 (C), 130.66, 128.80, 128.72, 128.54, 128.35, 128.16, 127.66, 127.34, 126.92, 124.11, 124.01, 117.13, and 116.46 (CH), 93.20 and 91.54 (C), 30.99 (*C*H$_2$Ph), 10.98 (Me). Anal. Calcd for $C_{34}H_{27}F_3N_2O_3PdS$: C, 57.76; H, 3.85; N, 3.96; S, 4.53. Found: C, 57.52; H, 3.84; N, 3.78; S, 4.48. Single crystals of **18a** were grown by liquid diffusion of diethyl ether into a solution of **18a** in 1,2-dichloroethane.

Synthesis of [Pd(η-C_9H_4Bn-1-Ph-2-Me-3)(tmeda)]TfO (18b). The brown complex **18b** was similarly prepared from **6b** (100 mg, 0.20 mmol), Tl(TfO) (73 mg, 0.20 mmol), and PhC≡CMe (0.050 cm^3, 0.40 mmol). Yield: 83 mg, 62%. Mp: 162 °C (dec). Λ_M (acetone): 139 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.5−7.4 (several m, 5 H, Ph-2-indenyl), 7.15−6.85 (several m, 9 H aromatic H's), 3.31 and 3.27 (AB system, 2 H, C*H*$_2$Ph, $^2J_{HH}$ = 15 Hz), 3.1−2.5 (m, 4 H, CH_2-CH_2), 2.91, 2.65, 2.63, and 2.54 (s, 3 H, MeN), 1.38 (s, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 136.13 (C), 135.17 (2 × C), 132.21 (C), 130.70 (C), 130.46, 129.14, 128.91, 128.55, 128.23, 127.97, 127.49, 126.86, 115.92, and 115.36 (CH), 90.82 and 88.86 (C), 61.40 (2 × C, CH_2CH_2), 52.01 and 51.80 (MeN), 51.33 (2 × C, MeN), 31.08 (*C*H$_2$Ph), 10.79 (Me). HR FAB MS: calcd for $C_{29}H_{35}N_2$Pd, *m*/*e* 515.1841 (31.6), 516.1851 (73.6), 517.1835 (100), 519.1839 (79.3), 521.1852 (37.2); found, *m*/*e* 515.1849 (35.2), 516.1861 (79.8), 517.1853 (100), 519.1843 (72.7), 521.1858 (43.8).

Synthesis of [Pd{η^3-CMe_2C\{C_6H(*E*-CH=CHPh)-6-$(OMe)_3$-2,3,4\}CH_2\}(tmeda)]TfO (19). 3-Methyl-1,2-butadiene (34 mg, 0.50 mmol) was added to a suspension of **3b** (120 mg, 0.23 mmol) and Tl(TfO) (81 mg, 0.23 mmol) in CH_2Cl_2 (5 cm^3). The mixture was stirred for 20 h and filtered over anhydrous $MgSO_4$. The solution was concentrated to 1 cm^3 and chromatographed. Elution with chloroform−acetone (1:1) rendered colorless **19**. Yield: 71 mg, 44%. Mp: 196−198 °C. Λ_M (acetone): 110 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 7.25−7.48 (m, 5 H, C_6H_5), 7.05 (d, 1 H, CH=CH, ^3J = 16 Hz), 6.96 (s, 1 H, aryl-H), 6.94 (d,1 H, CH=CH, ^3J = 16 Hz), 4.04, 3.96 and 3.87 (s, 3 H, MeO), 3.68 (d, 1 H, allyl-C*H*$_2$, $^2J_{HH}$ = 1 Hz), 3.45 (d, 1 H, allyl-C*H*$_2$, $^2J_{HH}$ = 1 Hz), 2.80−3.00 (m, 4 H, CH_2CH_2), 3.04, 2.86, 2.82, and 2.61 (s, 3 H, MeN), 1.47 and 1.06 (s, 3 H, allyl-*C*H$_3$). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 153.57, 149.36, 141.28, 136.57, and 132.84 (C-aryl), 131.12, 128.82, 128.09, 126.28, and 124.61 (CH-aryl and CH=CH), 126.32 and 120.61 (C-allyl and C-aryl), 104.45 (aryl *C*H), 84.42 (*C*Me$_2$), 61.86 (MeO), 61.31 (CH_2CH_2), 60.83 (MeO), 59.86 (CH_2CH_2), 57.35 (allyl-*C*H$_2$), 55.97 (MeO), 52.07, 51.75, 50.31, and 49.40 (MeN), 23.87 and 23.14 (allyl-*C*H$_3$). Anal. Calcd for $C_{29}H_{41}F_3N_2O_6PdS$: C, 49.12; H, 5.83; N, 3.95. Found: C, 49.46; H, 5.84; N, 3.96.

Synthesis of [Pd{S_2C\{C_6H(*E*-CH=CHPh)-6-$(OMe)_3$-2,3,4\}\](tmeda)]TfO (20). Carbon disulfide (47 mg, 0.62 mmol) was added to a suspension of **3b** (120 mg, 0.23 mmol) and Tl(TfO) (81 mg, 0.23 mmol) in CH_2Cl_2 (5 cm^3). The intensely orange-colored mixture was stirred for 20 h and filtered over anhydrous $MgSO_4$. The solution was concentrated (1 cm^3), and diethyl ether was added to precipitate **20** as an orange solid. Yield: 147 mg, 90%. Mp: 175−176 °C. Λ_M (acetone): 113 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.34−7.54 (m, 6 H, C_6H_5 and C*H*=CH), 6.90 (d, 1 H, CH=C*H*, ^3J = 16 Hz), 6.86 (s, 1 H, aryl-H), 4.04, 4.00, and 3.90 (s, 3 H, MeO), 3.11 (s, 4 H, CH_2–CH_2), 2.85 (s, 12 H, MeN). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 214.26 (v w CS_2, tentative), 158.41, 153.04, 141.29, 136.44, and 136.21 (C-aryl), 132.13 (CH=CH or *p*-C_6H_5), 129.36 (C-aryl), 128.85 and 126.89 (*o*,*m*-C_6H_5), 128.56 and 126.32 (CH=CH and/or *p*-C_6H_5), 107.36 (aryl-*C*H), 61.29 (CH_2CH_2), 61.58, 60.96, and 56.42 (MeO), 50.20 (MeN). Anal. Calcd for $C_{25}H_{33}F_3N_2O_6PdS_3$: C, 41.87; H, 4.64; N, 3.91; S, 13.41. Found: C, 41.93; H, 4.78; N, 4.00; S, 13.34.

Synthesis of [Pd{S(NMe)C\{C_6H(*E*-CH=CHPh)-6-$(OMe)_3$-2,3,4\}\](tmeda)]TfO (21). The yellow complex **21** was similarly prepared from methyl isocyanate (35 mg, 0.48 mmol), **3b** (120 mg, 0.23 mmol), and Tl(TfO) (81 mg, 0.23 mmol). Yield: 102 mg, 63%. Mp: 142−143 °C. Λ_M (acetone): 121 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 7.30−7.60 (m, 5 H, C_6H_5), 7.14 (d, 1 H, C*H*=CH, ^3J = 16 Hz), 7.03 (d, 1 H, C*H*=CH, ^3J = 16 Hz), 6.95 (s, 1 H, aryl-H), 4.00, 3.97, and 3.89 (s, 3 H, MeO), 2.90−3.15 (s, 4 H, CH_2–CH_2), 2.99, 2.96, 2.82 (s, 3 H, MeN), 2.80 (s, 2 × MeN, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 194.95 (C=S), 155.47, 149.43, 141.29 and 136.56 (C-aryl), 131.48 (CH=CH or *p*-C_6H_5), 130.40 (C-aryl), 128.87 (*o*,*m*-C_6H_5), 128.31 (CH=CH or *p*-C_6H_5), 126.75 (*o*, *m*-C_6H_5), 124.13 (C-aryl), 124.05 (CH=CH or *p*-C_6H_5), 104.08 (aryl-*C*H), 61.80 and 61.75 (CH_2CH_2), 61.69, 61.02, and 56.09 (MeO), 51.73, 51.66, 50.81, and 50.75 (Me_2N), 36.82 (MeN). Anal. Calcd for $C_{26}H_{36}F_3N_3O_6PdS_2$: C, 43.73; H, 5.08; N, 5.88; S, 8.98. Found: C, 43.61; H, 5.15; N, 6.01; S, 9.34.

X-ray Structure Determinations. Crystal data are given in Table 1. Crystals were mounted on glass fibers in inert oil and transferred to the cold gas stream of the diffractometer. Data were collected in ω-scan mode using Mo Kα radiation (λ = 0.710 73 Å). Structures were solved by direct methods and refined anisotropically against F^2 (program SHELXL-93 for 12, otherwise SHELXL-97, G. M. Sheldrick, University of Göttingen, Göttingen, Germany). Hydrogen atoms were included using a riding model or rigid methyl groups. Special features of refinement: In **12** and **18a** the triflate anions are disordered over two positions; in **17b** the TMEDA ligands (excluding N atoms) and the ring C21−26 are similarly disordered. In all cases an extensive system of restraints (to light atom displacement factors, local ring symmetry, and similarity of disorder components) was employed to ensure stability of refinement. Compound **18a** crystallizes as a diethyl ether hemisolvate.

Results and Discussion

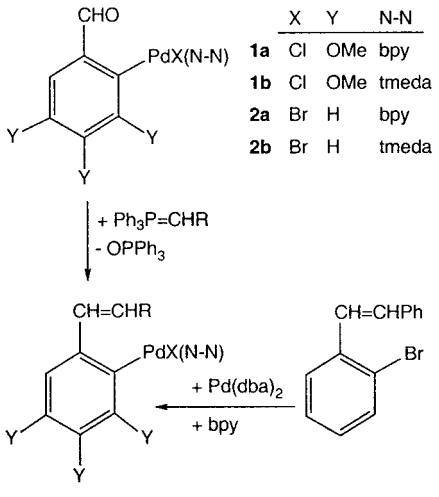
Wittig Reactions. The reactions of 2-formylaryl complex **1** or **2** with ylides Ph_3P=CHR [R = Ph, py (2-pyridyl), Cl] led to 2-(2′-R-vinyl)aryl complexes **3**−**5** or **6**, respectively (see Scheme 2). The ylides were generated in situ by reacting the corresponding phosphonium

Table 1. Summary of X-ray Data for Complexes 12, 17b, and 18a

	compound		
	12	**17b**	**18a·0.5C$_4$H$_{10}$O**
formula	$C_{28}H_{37}F_3N_2O_7PdS$	$C_{29}H_{33}F_3N_2O_3PdS$	$C_{36}H_{32}F_3N_2O_{3.5}PdS$
M_r	709.06	653.03	744.10
habit	red-brown prism	brown tablet	red cube
cryst size (mm)	0.7 × 0.35 × 0.2	0.4 × 0.4 × 0.15	0.09 × 0.09 × 0.07
cryst system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$C2/c$
diffractometer	Siemens P4	Stoe STADI-4	Bruker SMART
cell constants			
a (Å)	13.5419(14)	10.414(2)	22.8471(14)
b (Å)	11.2163(14)	21.840(3)	16.2595(11)
c (Å)	21.111(2)	12.379(2)	18.5179(12)
β (deg)	102.819(8)	95.48(2)	111.016(2)
V (Å^3)	3126.7	2802.6	6421.5
Z	4	4	8
D_x (Mg m^{-3})	1.506	1.548	1.539
μ (mm^{-1})	0.72	0.79	0.71
abs corr, transms	ψ-scans, 0.74−0.88	ψ-scans, 0.69−0.77	SADABS, 0.81−0.98
F(000)	1456	1336	3032
T (°C)	100	130	130
2θ(max) (deg)	50	50	52.7
no. of reflcns			
measd	6107	5227	20 539
indepdt	5491	4940	6573
R_{int}	0.018	0.034	0.051
no. of params	390	322	454
no. of restraints	453	319	537
wR2[a]	0.122	0.114	0.107
R1[b]	0.044	0.052	0.041
S	1.04	1.05	0.94
max $\Delta\rho$ (e Å^{-3})	1.1	0.6	0.8

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for reflections with $I > 2\sigma(I)$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{0.5}$ 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.

Scheme 2



	X	Y	N-N
1a	Cl	OMe	bpy
1b	Cl	OMe	tmeda
2a	Br	H	bpy
2b	Br	H	tmeda

	X	Y	N-N	R	*E* : *Z*
3a	Cl	OMe	bpy	Ph	3 : 1[a]
3b	Cl	OMe	tmeda	Ph	only *E*
4	Cl	OMe	bpy	py[b]	4 : 1[a]
	Cl	OMe	tmeda	py[b]	only *E*[c]
5	Cl	OMe	tmeda	Cl	only *E*
6a	Br	H	bpy	Ph	2.6 : 1
6b	Br	H	tmeda	Ph	9 : 1[c]

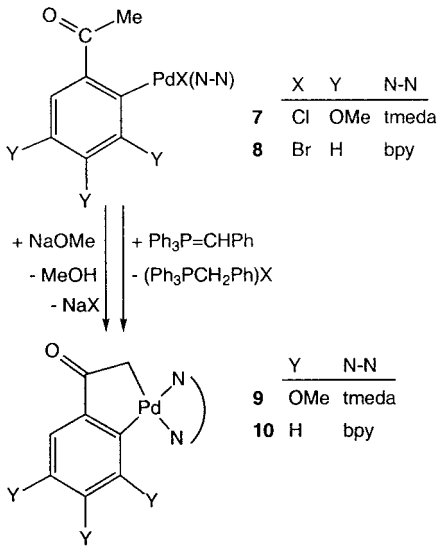
[a] Isolated pure *E* isomers. [b] py = 2-pyridyl. [c] See discusion.

chloride with ^{n}BuLi (1:1) (**3a**, **4**, **6**) or potassium *tert*-butoxide (**3b**, **5**). In addition, complex **6a** was prepared by an oxidative addition reaction of 2-bromostilbene to "Pd(dba)$_2$" in the presence of bpy (2,2′-bipyridine). This procedure offers a better yield and it is less laborious. Unfortunately, is was not possible to prepare **6b** using the same method. Complexes **3a**, **4**, and **6a**, containing the ligand bpy, were isolated as mixtures of the two stereoisomers [*E*:*Z* = 3:1 (**3a**), 4:1 (**4**), and 2.6:1 (**6a**), respectively], although it was possible to isolate the most abundant *E*-**3a** and *E*-**4** by recrystallizing the corresponding mixtures. When the same ylides were reacted with the tmeda complex **1b**, complexes **3b** and the analogue to **4** were obtained with complete regioselectivity toward the *E* isomer−the *Z* isomer was not observed in the crude product−independently of the method used for the formation of the ylide: ^{n}BuLi/(BnPh$_3$P)Cl or NaOMe/(BnPh$_3$P)Cl. However, although the tmeda complex analogous to **4** could be isolated spectroscopically pure, good elemental analysis for carbon could not be obtained. (Anal. Calcd for $C_{22}H_{32}ClN_3O_3Pd$: C, 50.01; H, 6.10; N, 7.95. Found: C, 49.19; H, 6.02; N, 7.54.) If the same reaction is carried out from the tmeda complex **2b**, the complex **6b** is obtained as isomeric mixtures with variable *E*:*Z* ratios (range 2:1 to 9:1).

It is known that semistabilized ylides, such as those used in these reactions, react with organic carbonyl compounds to give ca. 1:1 *E*:*Z* mixtures.[50] One of the mechanistic proposals for the Wittig reaction involves the formation of oxaphosphetanes (OPA).[50] Very recent calculations suggest that, in the case of semistabilized ylides, planar transition states (TS's), which would give a trans OPA, are 2.1 kcal more stable than a puckered transition state leading to a cis OPA.[51] Moreover, in our

(50) Johnson, A. V. *Ylides and Imines of Phosphorus*; J. Wiley & Sons: New York, 1993.

Scheme 3



case, the examination of simple models shows a sterical hindrance between the metallic moiety and the phenyl substituents of the ylidic group (PPh_3 and CHPh) in the cis OPA's or TS's, whereas it decreases markedly in the trans case. Thus a steric effect could be responsible of the observed regioselectivity favoring the *E* geometry. In these cases, the presence of the methyl substituents of the tmeda ligand enhances the steric hindrance between the metallic fragment and the ylidic Ph groups (PPh_3 and CHPh) in the cis OPA's and TS's, increasing the energy differences between both possibilities and favoring even more the *E* geometry of the alkenyl group. A further example is the reaction of **1b** with $Ph_3P{=}CHCl$, which gives also exclusively the *E* isomer [Pd{C_6H(*E*-CH=CHCl)-6-$(OMe)_3$-2,3,4}Cl(tmeda)] (**5**).

The spectroscopic data for complexes **3**−**6** are in accordance with the proposed structures. A useful tool has been the study of the signals corresponding to the −CH=CH− group. In the case of complexes **3**, **4**, and **6**, these hydrogens appear as two doublets with $^3J_{HH}$ = 16 Hz for the *E* isomers and $^3J_{HH}$ = 12 Hz for the *Z* isomers. Complex **5** shows $^3J_{HH}$ = 13.5 Hz, which corresponds to an *E* disposition since the presence of a chloro substituent in a CH=CH grouping causes a lowering of these coupling constants.[52]

The *o*-acetylcomplexes [Pd{C_6H(C(O)Me)-6-$(OMe)_3$-2,3,4}Cl(tmeda)] (**7**) [prepared by reacting [Pd(κ^2-{C_6H-(C(O)Me)-6-$(OMe)_3$-2,3,4})(μ-Cl)]$_2$ with tmeda] and [Pd-{C_6H_4(C(O)Me)-2}Br(bpy)] (**8**)[2] reacted differently with $Ph_3P{=}CHPh$, since it acts as a base deprotonating the acetyl methyl groups and forming the 3-palladaindan-1-ones [Pd(κ^2-{C_6H(C(O)CH_2)-6-$(OMe)_3$-2,3,4})(tmeda)] (**9**) and [Pd(κ^2-{C_6H_4(C(O)CH_2)-2})(bpy)] (**10**). These syntheses are improved by reaction of **7** and **8** with NaOMe as a base (Scheme 3). The crystal structure of **9** has been previously communicated.[7] As far as we are aware, these are the only examples of isolated and characterized 3-palladaindan-1-ones.[6]

Reactions with Alkynes. Formation of Indenylpalladium Complexes. Arylpalladium complexes react with alkynes to give mono-, di- and triinserted derivatives (see Scheme 1)[8−18] or, after depalladation, organic compounds such as spirocycles,[9,19] indenols, indenones,[20] carbocycles,[9,21−26] and oxygen,[27−29] sulfur,[30−32] or nitrogen heterocycles.[13,14,24,27,28,33−38] In some cases, the palladation reaction and the insertion of the alkyne are part of a catalytic cycle yielding interesting organic compounds.[26,53−64] This explains the present interest of this topic.

We have recently reported four indenyl complexes with Y = OMe (L_2 = tmeda, R = R′ = H, Ph; R = H, R′ = Ph; L_2 = bpy, R = R′ = Me) (Scheme 1).[39] obtained from the reactions of (2,3,4-trimethoxy-6-alkenylaryl)-palladium complexes with alkynes. To explore the limits of this method we have extended the study to other alkynes and (*o*-alkenylaryl)palladium complexes. Thus, when complex **3b** is reacted with excess of alkynes RC≡CR′ [R = R′ = Me, Et, R = H, R′ = C(O)Me] in the presence of TlOTf (1:3−2:1 molar ratios), an annulation process takes place with the formation of the indenylpalladium derivatives **11** and **12**, the latter being the only regioisomer observed in the reaction (see Scheme 4). This method constitutes an easy synthesis of indenyl palladium complexes, because, in contrast to the traditional method, it requires neither precautions against air and moisture nor the synthesis of the family of R,R′-indenes. Because the above and previous examples involved Y = OMe,[39] we investigated the reactions of 2-palladastilbenyl complexes 6a,b (Y = H) with a family of symmetrical (R = R′ = H, Me, Et, Ph) and unsymmetrical (R = Ph, R′ = H, Me) alkynes. Again, these reactions result in the formation of the indenyl complexes **13**−**18** (Scheme 4) in yields 53−83%. The reaction of the bpy complex **6a** with PhC≡CH gives a 1.5:1 mixture of regioisomers **17a** and **17a′**, respectively; however, the tmeda complex **6b** gives **17b** as the only regioisomer. Here, as in the case of the Wittig reactions commented above, replacing bpy by tmeda results in a greater selectivity. The formation of **17b** results from the insertion of PhC≡CH into the C−Pd bond in such a way that the CPh moiety is attached to the carbon atom previously coordinated to Pd (C_{Pd}); the same regioselectivity was found in the reaction of **3b** with PhC≡CH.[39] However, in the insertion of PhC≡CMe the group attached to C_{Pd} is CMe.

It is reasonable to assume that these reactions occur through the insertion of the alkyne into the aryl C−Pd bond forming an alkenylpalladium intermediate A

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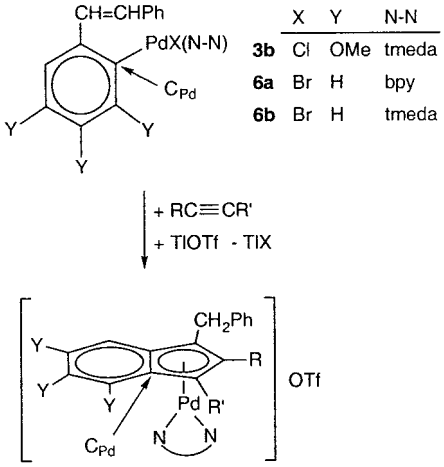
Scheme 4

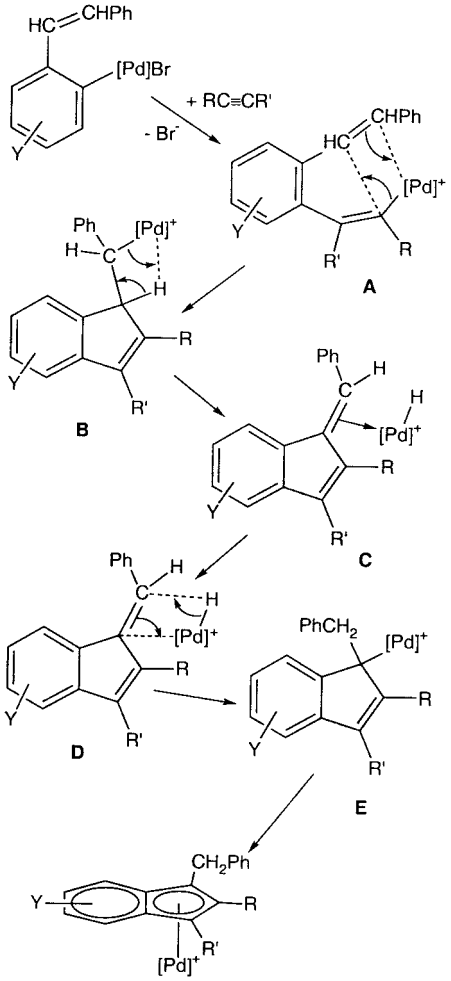


	X	Y	N-N
3b	Cl	OMe	tmeda
6a	Br	H	bpy
6b	Br	H	tmeda

	Y	N-N	R	R'
11	OMe	tmeda	Me	Me
12	OMe	tmeda	C(O)Me	H
13a	H	bpy	H	H
13b	H	tmeda	H	H
14a	H	bpy	Me	Me
14b	H	tmeda	Me	Me
15a	H	bpy	Et	Et
15b	H	tmeda	Et	Et
16a	H	bpy	Ph	Ph
16b	H	tmeda	Ph	Ph
17a	H	bpy	H(Ph)	Ph(H)
17b	H	tmeda	H	Ph
18a	H	bpy	Ph	Me
18b	H	tmeda	Ph	Me

(Scheme 5); this behavior is well-documented.[8,65,66] Addition of the C−Pd bond to the alkenyl substituent, a well-known process occurring in palladium-catalyzed cyclization reactions,[67] would give the alkylpalladium complex **B**. The successive β-hydride elimination, to give the hydrido benzofulveno π-complex **C**, and readdition through **D** to give a three-coordinated σ-indenyl complex **E** should lead to the more stable η-indenyl complexes **11**−**18** (Scheme 5).[39] According to this pathway, the observed regioselectivity of the reaction with MeC(O)C≡CH, PhC≡CH, or PhC≡CMe (Scheme 4) must be determined in the alkyne insertion step. We have previously proposed an empirical scale that gives the tendency of the CR′ moiety of an alkyne RC≡CR′ to be attached to C_{Pd}; this scale was based on data from the literature relative to catalytic and stoichiometric reactions involving alkynes and arylpalladium species:[68] $CO_2Et \approx CHO \approx C(O)Me \approx SO_2C_6H_4Me\text{-}4 \geq H > Me \approx Et > aryl > Bu^t \approx SiR_3$. Because the regioselectivity in the formation of **17b** and **18a,b**, as well as that previously found in the reaction of PhC≡CH with complex **3b**,[39] did not follow such a scale but instead showed Me > Ph > H, we have reconsidered this series. We notice

Scheme 5



that the position of H in the scale was based only in a work by Liao and Cheng.[62] These authors proposed a mechanism that does not include an insertion step of the alkyne into the C−Pd bond. This seems also to happen in the recently reported palladium-catalyzed synthesis of indoles,[56,69] benzofurans,[55] and azaindols.[70] Consequently, the above scale must be corrected to be the following: $CO_2Et \approx CHO \approx C(O)Me \approx SO_2C_6H_4\text{-}Me\text{-}4 > Me \approx Et > aryl > Bu^t \approx SiR_3 > H$. If we accept this new order, only the synthesis of **12** remains an exception.

The results of our reactions are independent of the *E* and/or *Z* nature of the styryl substituent, as we had noted previously,[39] which agrees with our proposed pathway.

We have attempted similar reactions with (2-vinylaryl)palladium complexes $[Pd\{C_6H_4(CH{=}CH_2)\text{-}2\}Br(PR_3)_2]$ (R = Ph, C_6H_4Me-4), but no indenylderivatives are formed and, instead, decomposition gave a mixture of organic materials.

Reactions with Cumulenes. The complex **3b** reacts with $CH_2{=}C{=}CMe_2$ to give the η^3-allyl complex $[Pd(\eta^3\text{-}CMe_2C\{C_6H(E\text{-}CH{=}CHPh)\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}CH_2)(tmeda)]TfO$ (**19**) (Scheme 6). This is an expected result since

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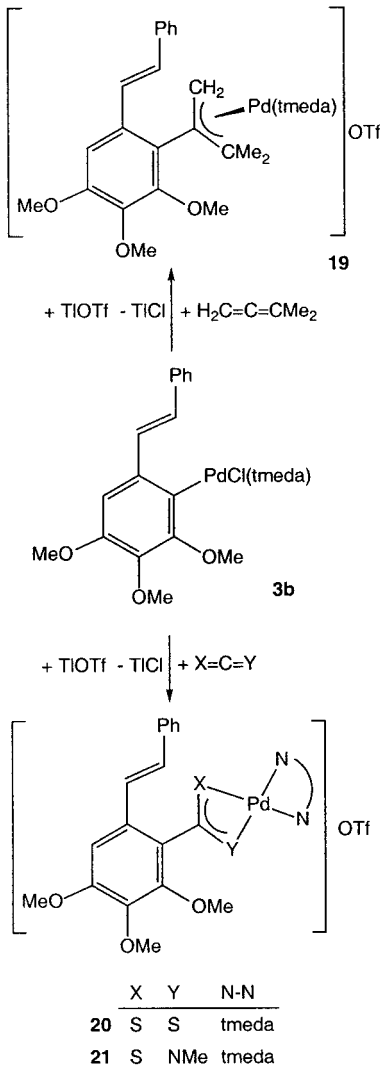
Scheme 6



similar reactions are known and constitute a simple route to allylpalladium complexes.[71−74] Moreover, insertion of allenes into carbon−palladium bonds to give allylpalladium species is very probably a key step in many palladium-catalyzed reactions involving allenes.[75−81]

We have also tested with other cumulenes similar reactions that could result in the formation of heterocycles.[82] Thus, we carried out reactions of **3b** with CS_2 and MeN=C=S in the presence of TlOTf; however, they result in the formation of [Pd(S_2C\{C_6H(*E*-CH=CHPh)-6-$(OMe)_3$-2,3,4\})(tmeda)]TfO (**20**) and [Pd(SC\{C_6H(*E*-CH=CHPh)-6-$(OMe)_3$-2,3,4\}NMe)(tmeda)]TfO (**21**), respectively (Scheme 6). We are only aware of one example of insertion of CS_2 into a Pd−C bond−that starting from [PdI(Me)(PMe_3)$_2$] and giving a dithioacetate complex[44,45] and none for MeN=C=S. The ^{13}C NMR spectrum of **20** shows a weak signal at 214.26 ppm, which may be assignable to the CS_2 grouping of a η^2-dithiocarboxylate ligand.[82] Complex **21** exhibits a signal at 194.95 ppm that should be associated with the quaternary carbon of the η^2-SC(NMe) group.

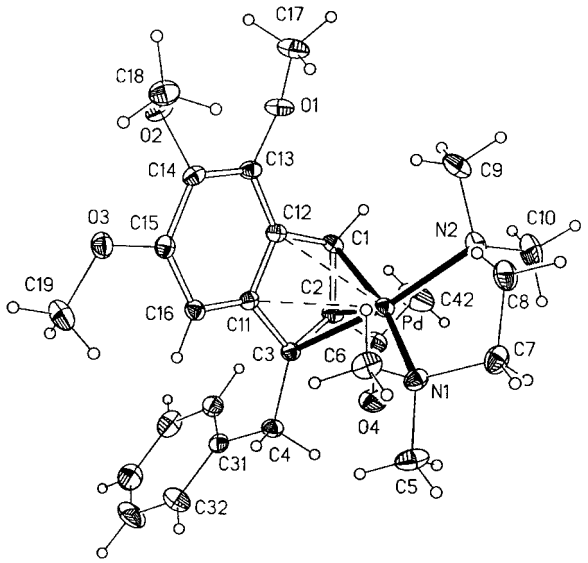


Figure 1. Thermal ellipsoid plot of the cation of complex **12** (30% probability levels) with the labeling scheme. Selected bond lengths (Å) and angles (deg): Pd−N(1) 2.115(3), Pd−N(2) 2.112(4), Pd−C(1) 2.185(4), Pd−C(2) 2.175(4), Pd−C(3) 2.220(4), C(41)−O(4) 1.213(5); N(1)−Pd−N(2) 84.64(14).

The reactions of the compounds **6a,b** with these cumulenes, under the same conditions, result in the formation of ill-defined mixtures.

X-ray Structure Determinations. The crystal and molecular structures of the indenyl complexes **12**, **17b**, and **18a** have been determined by X-ray diffraction studies (see Figures 1−3 and Table 1). The crystal structure of **3b** was reported in a preliminary communication.[7] In complex **12** the distances of Pd to the "allylic" carbons C(1) [2.185(4) Å], C(2) [2.175(4) Å], and C(3) [2.220(4) Å] are significantly shorter than those to the "ene" carbons C(11) [2.567(4) Å] and C(12) [2.547(4) Å]. However these differences are not enough to support a η^3 formulation for the indenyl ligand since the ΔMC value (difference beween the average of the metal−carbon distances to the "allyl" and "ene" carbons)[83,84] of 0.36 Å lies between those corresponding to η^3 (0.5−0.9 Å) and those expected for η^5 coordination (0−0.2 Å).[83−89] Similar intermediate values are observed for the fold

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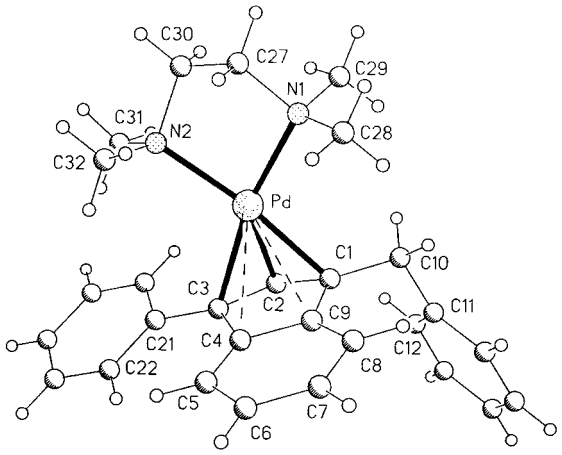

Figure 2. The cation of complex **17b** with the labeling scheme. Only one position of the disordered groups is shown. Selected bond lengths (Å) and angles (deg): Pd−N(1) 2.143(4), Pd−N(2) 2.143(5), Pd−C(1) 2.204(5), Pd−C(2) 2.157(6), Pd−C(3) 2.244(5); N(1)−Pd−N(2) 83.42(17).

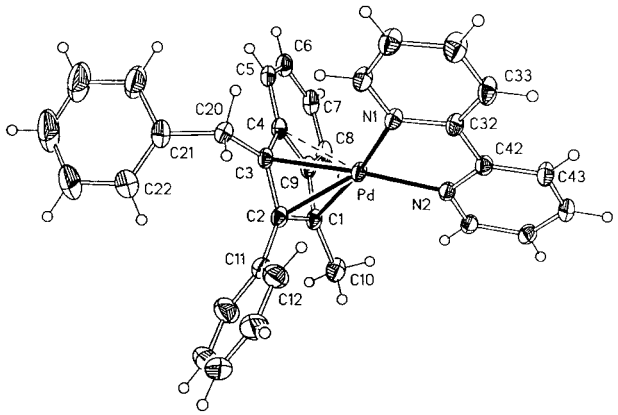

Figure 3. Thermal ellipsoid plot of the cation of complex **18a** (30% probability levels) with the labeling scheme. Selected bond lengths (Å) and angles (deg): Pd−N(1) 2.091(3), Pd−N(2) 2.096(3), Pd−C(1) 2.211(3), Pd−C(2) 2.167(4); N(1)−Pd−N(2) 78.59(12).

angle (dihedral angle between the plane defined by the three "allylic" carbons and that formed by the benzenoid carbons)[89,90] with a value of 11.2° (20−29° for η^3, 7−10° for η^5) [87,89] and the slip angle (the angle between the normal to the plane through the metal atom and the centroid−metal vector)[83,84,87] with 13.2° (20−24° for η^3, 2−5° for η^5).[84,87] However, the slip distortion (distance between the C5 centroid and the projection of the metal atom on this ring)[83,84,87] of 0.46 Å could correspond to a η^3 situation (>0.3 Å).[84] In consequence, and as we have observed previously in similar indenylpalladium complexes,[39] we conclude that the hapticity of the indenyl ligand is intermediate between η^3 and η^5. Very recently, an indenylpalladium complex has been described and the authors have found a similar ambiguity in establishing the hapticity of this ligand.[43]

In the case of the compounds **17b** and **18a** the data are also ambiguous but it is possible to observe a tendency toward a "more η^3 character": ΔMC 0.41 and 0.42 Å, fold angles 17.7 and 14.5°, slip angles 15.0 and 15.8°, and slip distortions 0.52 and 0.55 Å, respectively. Furthermore, the distances between the palladium atom and the "ene" carbons are longer for **17b** and **18a** (average: 2.603 and 2.630 Å) than for **12** (2.557 Å).

Conclusions

The synthesis of (*o*-alkenylaryl)palladium complexes, which could be of interest in the fields of nonlinear optics or organometallic polymers, is reported using two different methods, namely, oxidative addition or Wittig reactions. The latter represents one of the scarce examples of reaction of a phosphorus ylide with a carbonyl compound coordinated to a metal. In some cases, this reaction leads to the first 3-palladaindan-1-ones. Some of the (*o*-alkenylaryl)palladium complexes have been reacted with symmetrical and unsymmetrical alkynes to give, without precautions against air or moisture, a familly of highly substituted indenylpalladium complexes. A new scale for the regioselectivity of the insertion of alkynes into the C−Pd bond of arylpalladium complexes is reported. Finally, an (*o*-alkenylaryl)palladium complex has been shown to react with $CH_2{=}C{=}CMe_2$ to give η^3-allyl complex or with CS_2 or MeN=C=S, in the presence of TlOTf, to give the insertion product.

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Supporting Information Available: Tables of atomic positional parameters, bond lengths and interbond angles, atomic displacement parameters, and hydrogen atom parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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