Palladium-Assisted Formation of Carbon−Carbon Bonds. 4.[1] Synthesis and Reactivity of a Water-Soluble (2,3,4-Trimethoxy-6-(ethoxymethyl)phenyl)palladium(II) Complex. Reactions with Alkynes of Its Derivatives: Further Insight into the Pathway of Formation of Highly Functionalized Organic Spirocycles and X-ray Structures of Model Intermediates

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Mercuration of 3,4,5-trimethoxybenzyl chloride with mercury(II) acetate in ethanol, and further addition of aqueous NaCl, affords the compound [Hg(Ar)Cl] (**1**) [Ar = $C_6H(CH_2OEt)$-6-$(OMe)_3$-2,3,4], which reacts with $(Me_4N)Cl$ to give $[Hg(Ar)_2]$ (**2**). Complex **2** reacts with $K_2[PdCl_4]$ in water/acetone to give solutions from which, after addition of 2,2′-bipyridine (bpy), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) or pyridine (py), complexes [Pd(Ar)Cl(bpy)] (**3**), [Pd(Ar)Cl(tmeda)] (**4**), or *trans*-$[Pd(Ar)Cl(py)_2]$ (**5**), respectively, can be isolated. Complex **3** reacts with PPh_3 and $NaClO_4$ to give $[Pd(Ar)(bpy)(PPh_3)]ClO_4$ (**6**). Treatment of **5** with $AgClO_4$ and py affords $[Pd(Ar)(py)_3]ClO_4$ (**7**), which reacts with PPh_3 to give *cis*-$[Pd(Ar)(py)_2(PPh_3)]ClO_4$ (**8**). A comparative study of the reactions of **3**-**5** with various alkynes has been carried out. Thus, **3** reacts with $Tl(CF_3SO_3)$ and EtC≡CEt or with $AgClO_4$ and PhC≡CPh to give the (π-allyl)palladium complex (η^3-10-(ethoxymethyl)-6,7,8-trimethoxy-1,2,3,4-tetraethylspiro[4.5]-1,3,6-decatrien-8-enyl)(bpy)palladium(II) trifluoromethanosulfonate (**9**) or the monoinserted complex [Pd{*cis*-C(Ph)═C(Ph){$C_6H(CH_2OEt)$-6-$(OMe)_3$-2,3,4}}(bpy)]ClO_4 (**10**), respectively. Complex **10** reacts with PPh_3 giving [Pd{*cis*-CPh═CPh-(Ar)}(PPh_3)(bpy)]ClO_4 (**14**). Complex **4** reacts with $Tl(CF_3SO_3)$ and $MeO_2CC{\equiv}CCO_2Me$ or EtC≡CEt yielding the vinyl-substituted complex [Pd{*cis*-C(CO_2Me)═C(CO_2Me){$C_6H(CH_2OEt)$-6-$(OMe)_3$-2,3,4}}(tmeda)]CF_3SO_3 (**11**) or the spirocyclic compound 10-(ethoxymethyl)-6,7-dimethoxy-1,2,3,4-tetraethylspiro[4.5]-1,3,6,9-decatetraen-8-one (**12a**). When **5** reacts with EtC≡CEt, PhC≡CPh, or ToC≡CTo (To = C_6H_4Me-4), in the presence of $Tl(CF_3SO_3)$ or $AgClO_4$, the corresponding spirocyclic compounds **12a, 12b** (tetraphenyl), or **12c** (tetratolyl), respectively, are obtained, whereas the reaction with $MeO_2CC{\equiv}CCO_2Me$ gives the diinserted complex *trans*-[Pd{*cis*,*cis*-C(CO_2Me)═C(CO_2Me)C(CO_2Me)═C(CO_2Me)(Ar)}{$OS(O)_2CF_3$}$(py)_2$] (**13**). The structures of compounds **6**, **11**, **12c**, and **13** have been determined by X-ray diffraction.

The synthesis of spirocyclic compounds is of interest in the chemistry of natural[2] and pharmaceutical products. Thus, formation of a spiro compound is a key step in the synthesis of fredericamycin A, an important compound for the chemotherapy of human cancers.[3] However, these syntheses usually require specially designed starting materials and complicated multistep processes. Some catalytic[4] and a few stoichiometric[5] reactions using palladium compounds have recently been reported to give spirocycles. We have reported on the synthesis of (trimethoxyaryl)palladium complexes[6] and their uses in organic synthesis.[7] Spe-

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cifically, (6-acetyl-2,3,4-trimethoxyphenyl)palladium complexes react with diarylalkynes to give highly functionalized spirocyclic compounds (see Scheme 1).[1] In this paper we report the synthesis of new spirocyclic compounds.

Reactions of arylpalladium complexes with alkynes is a topic of current interest since they lead to new organopalladium complexes derived from the insertion of one, two or three alkynes into the Pd−C bond, or to organic compounds of various types.[8] Thus, for example, we have shown that (2,3,4-trimethoxyphenyl)-palladium complexes react with alkynes to give indenols or indenones when a formyl substituent is in the 6-position.[7a] However, benzofulvenes or spirocyclic compounds are obtained when the 6-acetyl derivative reacts with dialkyl- or diarylacetylenes, respectively (see Scheme 1).[1,7b] The marked influence of the nature of the 6-substituent prompted us to study the reactivity of (6-(ethoxymethyl)-2,3,4-trimethoxyphenyl)palladium complexes with various alkynes. One of the main differences between this study and those previously reported is that our does not involve a cyclopalladated complex as the starting material.

It is interesting to synthesize organic derivatives containing the trimethoxyphenyl group as it is frequently encountered in organic molecules of pharmaceutical interest, e.g. the antileukemic lactones steganacin and steganangin,[9] the antibacterial agent trimethoprim,[10] or the cytotoxic colchicine.[11]

In this paper, we report the first study on the reactivity of arylpalladium complexes with alkynes in relation to the nature of the neutral ligands attached to palladium. We have succeeded in isolating and characterizing a complete set of models for the intermediates in the synthesis of spirocyclic compounds.

Scheme 1

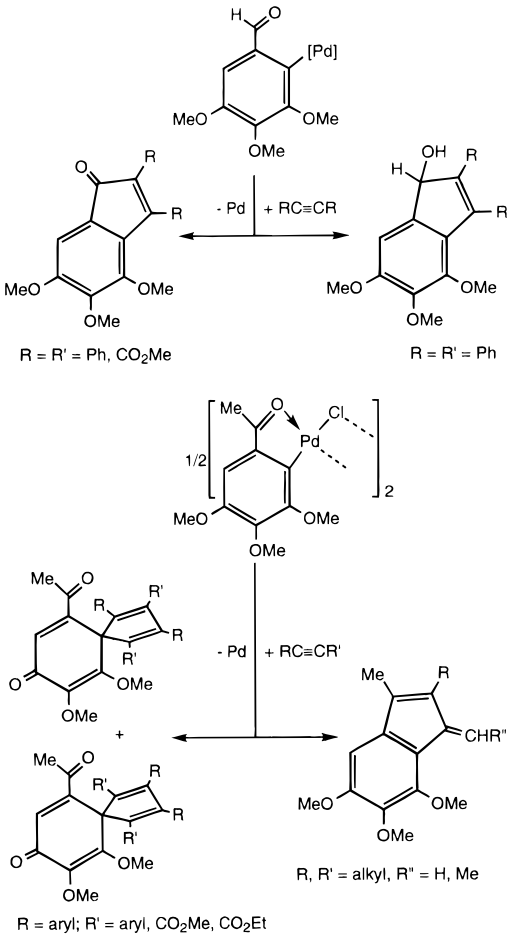
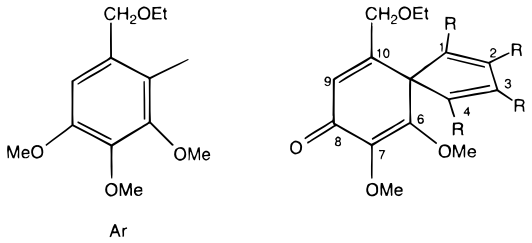


Chart 1



Experimental Section

Infrared spectra were recorded on a FT-IR Perkin-Elmer U-2000 spectrophotometer, in the range 4000−200 cm^{-1} using Nujol mulls between polyethylene sheets. ^1H and ^{13}C NMR spectra were recorded on a Brucker AC-200 or a Varian XL-300 spectrometer and referenced to internal $SiMe_4$. ^{31}P NMR spectra were measured on the Varian XL-300 machine with external H_3PO_4 reference. Some signals in the NMR spectra were assigned with the help of DEPT techniques. Conductivities were measured with a Phillips 9501 conductimeter. Melting points were determined on a Reichert apparatus and are uncorrected. C, H, N, and S analyses were carried out with a Carlo Erba EA 1108 microanalyzer with chromatographic separations. Solvents were distilled prior to use. The reactions were carried out at room temperature and without precautions to exclude atmospheric moisture unless otherwise stated. Chromatographic separations were performed using preparative-scale TLC plates prepared by us from commercial 60-mesh silica gel. Chart 1 shows the organic groups attached to the palladium atom and the numbering of the organic spirocyclic compounds prepared.

Synthesis of [Hg(Ar)Cl] (1). 3,4,5-trimethoxybenzyl chloride (5.0 g, 23.1 mmol) and $Hg(AcO)_2$ (7.4 g, 23.1 mmol) were

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mixed in ethanol (100 cm^3), and AcOH (*ca.* 0.5 cm^3) was added. The resulting solution was refluxed for 5 h and poured into aqueous NaCl (15 g in 300 cm^3); after 1 h of stirring, the white solid was filtered off, washed with water and hexane, and dried in air. Yield: 7.9 g, 74%. Mp: 144 °C. IR: ν(HgCl) 334 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, δ): 6.59 (s, HC_6, 1H), 4.44 (s, CH_2-aryl, 2H), 3.91 (s, *Me*O, 3H), 3.86 (s, *Me*O, 3H), 3.84 (s, *Me*O, 3H), 3.52 (q, $^3J_{HH}$ = 7 Hz, CH_2Me, 2H), 1.37 (t, *Me*CH_2, 3H). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): 155.9, 154.4, 140.8, 138.7, 132.5, 107.1 (*C*H-aryl) 72.7 (CH_2), 66.9 (CH_2), 61.1 (*Me*O), 60.7 (*Me*O), 56.1 (*Me*O), 15.2 (*Me*CH_2). Anal. Calc for $C_{12}H_{17}ClHgO_4$: C, 31.24; H, 3.71. Found: C, 31.40; H, 3.59.

Synthesis of [Hg(Ar)$_2$] (2). **1** (7.0 g, 15.2 mmol) and (NMe_4)Cl (2 g) were mixed in acetone (350 cm^3), refluxed for 4 h, and stirred overnight at room temperature. The solvent was evaporated and the residue treated with CH_2Cl_2 (300 cm^3) and anhydrous $MgSO_4$; the suspension was filtered over anhydrous $MgSO_4$ and the filtrate concentrated to *ca.* 20 cm^3. Addition of hexane precipitated **2** as a white solid. Yield: 3.4 g, 68%. Mp: 160 °C. ^1H NMR (200 MHz, $CDCl_3$, ppm): 6.81 (s, HC_6, 1H), 4.50 (s, CH_2-aryl, 2H), 3.94 (s, *Me*O, 3H), 3.88 (s, 2 × *Me*O, 6H), 3.59 (q, $^3J_{HH}$ = 7 Hz, CH_2Me, 2H), 1.21 (t, *Me*CH_2, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): 158.0, 153.1, 152.8, 141.3, 140.7, 108.5 (*C*H-aryl) 74.9 (CH_2), 65.6 (CH_2), 60.9 (*Me*O), 60.4 (*Me*O), 55.9 (*Me*O), 15.1 (*Me*CH_2). Anal. Calc for $C_{24}H_{34}HgO_8$: C, 44.27; H, 5.26. Found: C, 44.07; H, 5.26.

Synthesis of [Pd(Ar)Cl(bpy)] (3). A solution of **2** (358 mg, 0.55 mmol) in acetone (30 cm^3) was added to a solution of $PdCl_2$ (98 mg, 0.55 mmol) and NaCl (100 mg, 1.7 mmol) in water (12 cm^3), and the resulting mixture was stirred until all the solids dissolved (30 min). Evaporation of acetone precipitated **1**, and to the resulting aqueous solution bpy (87 mg, 0.55 mmol) and CH_2Cl_2 (16 cm^3) were added. After 30 min the organic layer was decanted and the aqueous solution extracted with CH_2Cl_2 (3 × 5 cm^3). The combined extracts were dried with anhydrous $MgSO_4$ and filtered. Partial evaporation of the solution (*ca.* 3 cm^3) and addition of diethyl ether gave **3** as a yellow solid. Yield: 264 mg, 92%. Mp: 208 °C. ^1H NMR (200 MHz, $CDCl_3$, ppm): 9.35−9.2, 8.1−7.8, 7.7−7.5, 7.3−7.2, and 6.75−6.60 (5 m, bpy, 8H), 6.77 (s, HC_6, 1H), 5.25, 4.85 (AB system, $^2J_{AB}$ = 11.7 Hz, CH_2-aryl, 2H), 4.10 (s, *Me*O, 3H), 3.91 (s, *Me*O, 3H), 3.87 (s, *Me*O, 3H), 3.52 ("q", $^3J_{HH}$ = 7 Hz, CH_2Me, 2H), 1.01 ("t", *Me*CH_2, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): 156.1, 154.1, 153.6, 152.1 (*C*H-bpy), 150.9, 149.2 (*C*H-bpy), 140.9, 139.2 (*C*H-bpy), 138.6 (*C*H-bpy), 137.5, 130.6, 126.5 (*C*H-bpy), 126.4 (*C*H-bpy), 122.2 (*C*H-bpy), 121.5 (*C*H-bpy), 107.2 (*C*H-aryl) 75.3 (CH_2), 65.7 (CH_2), 61.0 (*Me*O), 60.9 (*Me*O), 56.1 (*Me*O), 15.2 (*Me*CH_2). Anal. Calc for $C_{22}H_{25}N_2ClPdO_4$: C, 50.49; H, 4.81; N, 5.39. Found: C, 50.25; H, 4.84; N, 5.69.

Synthesis of [Pd(Ar)Cl(tmeda)] (4). The yellow solid **4** was prepared analogously to **3**, from $PdCl_2$ (310 mg, 1.75 mmol), KCl (410 mg, 5.5 mmol), **2** (1140 mg, 1.75 mmol), and tmeda (203 mg, 1.75 mmol). Yield: 609 mg, 72%. Mp: 145 °C. ^1H NMR (200 MHz, $CDCl_3$, ppm): 6.64 (s, HC_6, 1H), 5.41, 4.82 (AB system, $^2J_{AB}$ = 11 Hz, aryl-CH_2, 2H), 3.86 (s, *Me*O, 3H), 3.85 (s, *Me*O, 3H), 3.80 (s, *Me*O, 3H), 3.73 ("q", $^3J_{HH}$ = 7 Hz, CH_2Me, 2H), 2.8−2.5 (m, CH_2-tmeda, 4H), 2.69 (s, *Me*N, 3H), 2.67 (s, *Me*N, 3H), 2.59 (s, *Me*N, 3H), 2.40 (s, *Me*N, 3H), 1.31 ("t", *Me*CH_2, 3H). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, ppm): 154.6, 150.6, 140.7, 137.4, 127.6, 107.6 (*C*H-aryl), 76.2 (CH_2), 66.2 (CH_2), 63.1 (CH_2), 61.2 (*Me*O), 61.0 (*Me*O), 58.5 (CH_2), 56.0 (*Me*O), 51.8 (*Me*-tmeda), 51.0 (*Me*-tmeda), 48.3 (*Me*-tmeda), 47.8 (*Me*-tmeda), 15.6 (*Me*CH_2). Anal. Calc for $C_{18}H_{33}N_2ClPdO_4$: C, 44.73; H, 6.88; N, 5.79. Found: C, 44.64; H, 6.98; N, 5.81.

Synthesis of *trans*-[Pd(Ar)Cl(py)$_2$] (5). The white **5** was prepared analogously to **3** and **4** from $PdCl_2$ (98 mg, 0.55 mmol), KCl (100 mg, 5.5 mmol), **2** (358 mg, 0.55 mmol), and pyridine (*ca.* 0.5 cm^3). Yield: 277 mg, 97%. Mp: 119 °C. ^1H NMR (300 MHz, $CDCl_3$, ppm): 8.80 (m, *o-H*, pyridine 4H), 7.67 (m, *p-H*, pyridine, 2H), 7.19 (m, *m-H*, pyridine, 4H), 6.57 (s, HC_6, 1H), 4.99 (s, CH_2-aryl, 2H), 3.77 (s, *Me*O, 3H), 3.76 (s, *Me*O, 3H), 3.73 (s, *Me*O, 3H), 3.61 (q, ^3J = 7 Hz,CH_2Me, 2H), 1.24 (t, *Me*CH_2, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): 153.9, 153.7 (*C*H-py), 153.5, 137.5 (*C*H-py), 136.7, 124.9, 124.6 (*C*H-py), 124.0, 107.0 (*C*H-aryl) 75.1 (CH_2), 66.3 (CH_2), 60.7 (*Me*O), 60.2 (*Me*O), 55.9 (*Me*O), 15.5 (*Me*CH_2). Anal. Calc for $C_{22}H_{27}N_2ClPdO_4$: C, 50.30; H, 5.18; N, 5.33. Found: C, 49.96; H, 5.28; N, 5.33.

Synthesis of [Pd(Ar)(bpy)(PPh$_3$)]ClO$_4$ (6). Complex **3** (100 mg, 0.19 mmol), $NaClO_4$ (27 mg, 0.19 mmol), and PPh_3 (41 mg, 0.19 mmol) were mixed in CH_2Cl_2 (6 cm^3) and stirred for 1 h. The NaCl was filtered off and the resultant solution partially evaporated. Addition of diethyl ether resulted in the precipitation of yellow **6**. Yield: 148 mg, 92%. Mp: 219 °C. Λ_M (acetone): 121 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (200 MHz, $CDCl_3$, ppm): 8.72 (d, $^3J_{HH}$ = 8 Hz, bpy, 2H), 8.35−8.11 (m, bpy, 2H), 7.81−7.19 (m, PPh_3, 15H), 7.05 (m, bpy, 1H), 6.60 (s, HC_6, 1H), 4.57, 4.51 (AB system, $^2J_{AB}$ = 11 Hz, CH_2-aryl, 2H), 3.79 (s, *Me*O, 3H), 3.70 (s, *Me*O, 3H), 3.39 (s, *Me*O, 3H), 3.28 ("q", $^3J_{HH}$ = 7 Hz, CH_2Me, 2H), 0.85 ("t", *Me*CH_2, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): 155.8, 155.4, 152.4, 150.4, 150.3, 149.7 (CH), 141.5 (CH), 141.4 (CH), 136.4, 136.3, 135.25, 135.23, 134.7 (CH), 134.5 (CH), 131.6 (CH), 129.7, 129.0, 128.8 (CH), 128.7 (CH), 126.70 (CH), 126.68 (CH), 126.5 (CH), 124.9 (CH), 124.54 (CH), 124.51 (CH), 108.9 (*C*H-aryl), 75.5 (CH_2), 66.2 (CH_2), 60.4 (*Me*O), 60.1 (*Me*O), 56.3 (*Me*O), 14.9 (*Me*CH_2). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, ppm): 24.0. Anal. Calc for $C_{40}H_{40}N_2ClPPdO_8$: C, 56.54; H, 4.72; N, 3.29. Found: C, 56.44; H, 4.87; N, 3.29. Single crystals of **6** were obtained by liquid diffusion of diethyl ether into a solution of **6** in dichloromethane.

Synthesis of [Pd(Ar)(py)$_3$]ClO$_4$ (7). Complex **5** (100 mg, 0.19 mmol) was reacted with $AgClO_4$ (39 mg, 0.19 mmol) in acetone (6 cm^3) for 1 h. The suspension was filtered and pyridine (*ca.* 0.15 cm^3) added to the filtrate; the solution was partially evaporated and diethyl ether added to give white **7**. Yield: 81 mg, 64%. Mp: 150 °C dec. Λ_M (acetone): 130 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (200 MHz, $CDCl_3$, ppm): 8.65 (d, $^3J_{HH}$ = 5 Hz, pyridine *o*-H, 4H), 8.54 (d, $^3J_{HH}$ = 4.7 Hz, pyridine *o*-H, 2H), 7.6−8.0 (m, *p*-H, pyridine, 3H), 7.47 (m, *m*-H, pyridine, 2H), 7.32 (m, *m*-H, pyridine, 4H), 6.51 (s, HC_6, 1H), 4.96 (s, CH_2-aryl, 2H), 3.86 (s, *Me*O, 3H), 3.82 (q, ^3J = 7 Hz, CH_2Me, 2H), 3.76 (s, 2 × *Me*O, 6H), 1.32 (t, *Me*CH_2, 3H). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, ppm): 153.7, 152.4 (CH-py), 151.4, 149.7 (CH-py), 140.1, 139.0, 138.8 (CH-py), 136.7 (CH-py), 127.3, 126,3 (CH-py), 125.8 (CH-py), 107.7 (CH-aryl), 75.3 (CH_2), 66.4 (CH_2), 60.42 (MeO), 60.39 (MeO), 55.6 (MeO), 15.5 (MeCH_2). Anal. Calc for $C_{27}H_{32}N_3ClPdO_8$: C, 48.52; H, 4.83; N, 6.29. Found: C, 48.43; H, 4.86; N, 6.29.

Synthesis of *cis*-[Pd(Ar)(py)$_2$(PPh$_3$)]ClO$_4$ (8). Complex **7** (100 mg, 0.15 mmol) was reacted with PPh_3 (39 mg, 0.15 mmol) in refluxing acetone (6 cm^3) for 8 h. The solution was concentrated, and white **8** precipitated after diethyl ether addition. Yield: 65 mg, 50%. Mp: 104 °C. Λ_M (acetone): 126 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (300 MHz, $CDCl_3$, ppm): 8.6 (m, pyridine *o*-H, 2H), 8.38 (m, pyridine *o*-H, 2H), 7.8−7.0 (m, PPh_3 + py, 21H), 6.45 (s, HC_6, 1H), 4.80, 4.58 (broad AB system, CH_2-aryl, 2H), 3.77 (s, *Me*O, 3H), 3.74 (s, *Me*O, 3H), 3.95−3.49 (m, CH_2Me, 2H), 3.40 (s, *Me*O, 3H), 1.18 ("t", $^3J_{HH}$ = 7 Hz, *Me*CH_2, 3H). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, ppm): 152.2, 151.0, 150.4, 140.4, 138.2, 136.8, 136.7, 134.1, 133.9, 131.03, 130.98, 129.6, 128.7, 128.6, 128.5, 125.8, 107.7 (*C*H-aryl), 76.0 (CH_2), 66.4 (CH_2), 60.3 (*Me*O), 60.1 (*Me*O), 55.1 (*Me*O), 15.5 (*Me*CH_2). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, ppm): 28.4. Anal. Calc for $C_{40}H_{42}N_2ClPPdO_8$: C, 56.41; H, 4.97; N, 3.28. Found: C, 55.96; H, 5.05; N, 3.43.

Reaction of 3 with EtC≡CEt. Synthesis of 9. Complex **3** (100 mg, 0.19 mmol), $Tl(CF_3SO_3)$ (67 mg, 0.19 mmol), and EtC≡CEt (31 mg, 0.38 mmol) were mixed in CH_2Cl_2 (10 cm^3) and stirred for 1 h. The mixture was filtered and the filtrate evaporated to *ca.* 2 cm^3. Addition of diethyl ether rendered

yellow **9**. Yield: 88 mg, 58%. Mp: 114 °C. Λ_M (acetone): 110 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 8.6−8.8 (m, bpy, 2H), 8.5−8.6 (m, bpy, 1H), 8.2−8.4 (m, bpy, 3H), 7.8−7.65 (m, bpy, 1H), 7.65−7.5 (m, bpy, 1H), 5.65 (s, *H*C$_6$, 1H), 3.85 (s, *Me*O, 3H), 3.72 (s, *Me*O, 3H), 3.6−3.3 (m, Me*CH$_2$* O, 2H), 3.57 (s, *Me*O, 3H), 3.31, 3.00 (AB system, $^2J_{AB}$ = 13 Hz, C*H$_2$*-aryl, 2H), 2.95−2.2 (m, 3 × *CH$_2$*Me, 6H), 2.2−1.8 (m, *CH$_2$*-Me, 2H), 1.20−1.04 (m, 3 × *Me*CH$_2$, 9H), 1.03 ("t", $^3J_{HH}$ = 7 Hz, *Me*CH$_2$O, 3H), 0.92 ("t", $^3J_{HH}$ = 7.5 Hz, *Me*CH$_2$, 3H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, ppm): 154.5, 154.3, 150.8 (CH), 147.8, 147.6 (CH), 146.45, 141.3 (CH), 141.0 (CH), 139.4, 139.3, 127.35 (CH), 126.6 (CH), 124.6 (CH), 124.2 (CH), 119.3, 117.85, 70.1 (*C* spiro), 66.9 (Me*C*H$_2$O + *C*H$_2$-aryl), 62.2 (*Me*O), 60.1 (*Me*O), 56.1 (*Me*O), 20.9 (*C*H$_2$), 19.3 (*C*H$_2$), 19.1 (*C*H$_2$), 18.5 (*C*H$_2$), 15.0 (*Me*), 14.84 (*Me*), 14.76 (*Me*), 14.3 (*Me*), 14.05 (*Me*). Anal. Calc for $C_{35}H_{45}N_2F_3O_7PdS$: C, 52.46; H, 5.66; N, 3.49; S, 4.00. Found: C, 52.44; H, 5.66; N, 3.64; S, 3.70.

Reaction of 3 with PhC≡CPh. Synthesis of 10. Complex **3** (49 mg, 0.1 mmol) was reacted with $AgClO_4$ (20 mg, 0.1 mmol) and PhC≡CPh (17 mg, 0.1 mmol) in CH_2Cl_2 (6 cm^3) for 4 h. The AgCl was filtered off over Celite, the filtrate evaporated to *ca.* 2 cm^3, and diethyl ether added to give a precipitate of yellow **10**. Yield: 64 mg, 88%. Mp: 159 °C, dec. Λ_M (CH_2Cl_2): 36 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 8.9−8.5 (m, bpy, 1H), 8.3−7.4 (m, bpy, 3H), 7.4−6.9 (m, bpy, Ph, *H*C$_6$, 15H), 5.03, 4.62 (AB system, $^2J_{AB}$ = 8.5 Hz, C*H$_2$*-aryl, 2H), 3.90 (s, *Me*O, 3H), 3.65 (s, *Me*O, 3H), 3.48 ("q", $^3J_{HH}$ = 7 Hz, *CH$_2$* Me), 3.14 (s, *Me*O, 3H), 1.21 ("t", *Me*CH$_2$, 3H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, ppm): 158.1, 153.1, 152.6 (CH), 152.04, 151.97, 151.5, 149.3 (CH), 144.15, 140.9 (CH), 140.4, 140.3 (CH), 134.7, 131.3, 130.4, 129.1 (CH), 128.7 (CH), 128.6 (CH), 128.1 (CH), 127.6 (CH), 127.1 (CH), 126.6 (CH), 123.8 (CH), 122.7 (CH), 110.5 (*C*H-aryl), 77.7 (*C*H$_2$), 72.7 (*C*H$_2$-Me), 60.5 (*Me*O), 60.1 (*Me*O), 56.4 (*Me*O), 15.3 (*Me*CH$_2$). Anal. Calc for $C_{36}H_{35}N_2ClO_8Pd$: C, 56.48; H, 4.60; N, 3.67. Found: C, 56.45; H, 4.80; N, 3.73.

Reaction of 4 with MeO$_2$CC≡CCO$_2$Me. Synthesis of 11. Complex **4** (100 mg, 0.21 mmol), Tl(CF_3SO_3) (73 mg, 0.21 mmol), and MeO$_2$CC≡CCO$_2$Me (59 mg, 0.21 mmol) were reacted in CH_2Cl_2 (6 cm^3) for 1 h. The TlCl was filtered off, and the filtrate was concentrated to *ca.* 2 cm^3. Addition of diethyl ether resulted in the precipitation of yellow **11**. Yield: 121 mg, 79%. Mp: 125 °C. Λ_M (acetone): 120 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): ν(CO) 1716, 1706 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 6.98 (s, *H*C$_6$, 1H), 4.62, 4.09 (AB system, $^2J_{AB}$ = 9 Hz, C*H$_2$*-aryl, 2H), 4.2−4.1 (m, *CH$_2$*Me, 2H), 3.96 (s, *Me*O, 3H), 3.93 (s, *Me*O, 3H), 3.91 (s, *Me*O, 3H), 3.87 (s, CO$_2$*Me*, 3H), 3.70 (s, CO$_2$*Me*, 3H), 2.85 (s, *Me*N, 3H), 2.55 (s, *Me*N, 3H), 2.50 (s, *Me*N, 3H), 2.12 (s, *Me*N, 3H), 1.53 ("t", $^3J_{HH}$ = 7 Hz, *Me*CH$_2$, 3H), 2.15−2.36 and 2.5−2.7 (multiplets of tmeda CH$_2$, obscured). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, ppm): 170.4 (C=O), 168.2 (C=O), 161.6, 153.8, 151.1, 143.6, 129.7, 129.5, 126.3, 111.0 (*C*H-aryl), 75.9 (*C*H$_2$), 75.0 (*C*H$_2$), 65.0 (*Me*O), 61.0 (*Me*O), 60.8 (*Me*O), 58.1 (*C*H$_2$), 56.6 (*Me*), 55.1 (*C*H$_2$), 52.2 (*Me*) 52.1 (*Me*), 50.0 (*Me*), 49.4 (*Me*), 47.0 (*Me*), 15.6 (*Me*CH$_2$). Anal. Calc for $C_{25}H_{39}N_2F_3O_{11}PdS$: C, 40.62; H, 5.32; N, 3.79; S, 4.34. Found: C, 39.61; H, 5.31; N, 4.08; S, 4.34. Single crystals of **11** were obtained by liquid diffusion of diethyl ether into a solution of **11** in acetone.

Reaction of 4 with EtC≡CEt. Synthesis of the Spiro Compound 12a. Complex **4** (100 mg, 0.21 mmol), Tl(CF_3SO_3) (73 mg, 0.21 mmol), and EtC≡CEt (50 mg, 0.61 mmol) were reacted in CH_2Cl_2 for 24 h. The suspension was filtered over anhydrous $MgSO_4$, and the filtrate was concentrated and chromatographed. Elution with diethyl ether−hexane (1:1) rendered pale yellow **12a**. Yield: 31 mg, 39%. Mp: 39 °C. IR (Nujol): ν(CO) 1640 (br), 1690−1730 (br) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 6.61 (t, $^4J_{HH}$ = 1.5 Hz, *H*C$_6$, 1H), 3.89 (s, *Me*O, 3H), 3.75 (s, *Me*O, 3H), 3.56 (d, C*H$_2$*-aryl, 2H), 3.34 (q, $^3J_{HH}$ = 7 Hz, Me*CH$_2$*O, 2H), 2.4−1.7 (m, 4 × *CH$_2$*Me, 8H), 1.15 (t, *Me*CH$_2$O, 3H), 1.08 (t, $^3J_{HH}$ = 7.5 Hz, 2 × *Me*CH$_2$, 6H), 0.96 (t, $^3J_{HH}$ = 7.5 Hz, 2 × *Me*CH$_2$, 6H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, ppm): 185.0 (C=O), 161.1, 153.3, 147.7, 140.6, 139.4, 126.5 (*C*H-aryl), 68.5 (*C* spiro), 66.7 (*C*H$_2$O), 66.3 (*C*H$_2$O), 60.5 (*Me*O), 60.1 (*Me*O), 19.13 (*C*H$_2$Me), 19.08 (*C*H$_2$Me), 15.0 (*Me*CH$_2$O), 14.4 (*Me*CH$_2$), 13.8 (*Me*CH$_2$). Mass spectrum: *m*/*z* (% abundance) 375 (M$^+$ + 1, 13), 374 (M$^+$, 50), 299 (100), 288 (34), 141 (31), 129 (33), 128 (37), 115 (37), 91 (38), 57 (34), 55 (52). Tenacious solvents precluded satisfactory elemental analyses.

Reaction of 5 with Alkynes. Synthesis of 12a−c. Complex **5** (100 mg, 0.19 mmol), EtC≡CEt (50 mg, 0.61 mmol), and Tl(CF_3SO_3) (67 mg, 0.19 mmol) were reacted in CH_2Cl_2 (6 cm^3) for 24 h. The suspension was filtered over anhydrous $MgSO_4$ and the filtrate chromatographed; elution with diethyl ether/hexane (1:1) gave yellow **12a**. Yield: 39 mg, 55%.

12b was similarly prepared from **5** (100 mg, 0.19 mmol), PhC≡CPh (68 mg, 0.38 mmol), and $AgClO_4$ (39 mg, 0.19 mmol) as a yellow solid. Yield: 49 mg, 45%. Mp: 195 °C. IR (Nujol): ν(CO) 1658 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 7.3−6.7 (m, 4 × Ph, 20H), 6.61 (t, $^4J_{HH}$ = 1.5 Hz, *H*C$_6$, 1H), 4.09 (d, C*H$_2$*-aryl, 2H), 3.87 (s, *Me*O, 3H), 3.45 (s, *Me*O, 3H), 3.35 (q, $^3J_{HH}$ = 7 Hz, Me*CH$_2$* O, 2H), 1.15 (t, *Me*CH$_2$O, 3H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, ppm): 184.4 (C=O), 160.0, 151.2, 148.2, 142.9, 140.6, 134.9, 134.0, 129.9 (*C*H), 129.0 (*C*H), 128.1 (*C*H), 128.0 (*C*H), 127.6 (*C*H), 127.5 (*C*H), 127.3 (*C*H), 69.8 (*C* spiro), 67.3 (*C*H$_2$), 66.9 (*C*H$_2$), 60.9 (*Me*O), 60.4 (*Me*O), 15.2 (*Me*CH$_2$). Anal. Calc for $C_{39}H_{34}O_4$: C, 82.67; H, 6.05. Found: C, 82.65; H, 6.13. Mass spectrum: *m*/*z* (% abundance) 567 (M$^+$ + 1, 45), 566 (M$^+$, 100), 178 (16), 167 (30), 135 (28), 105 (PhCO$^+$, 42), 91 (18), 77 (Ph$^+$, 26), 59 (16).

A similar procedure was used for preparing **12c** from **5** (100 mg, 0.19 mmol), ToC≡CTo (79 mg, 0.38 mmol), and Tl(CF_3SO_3) (67 mg, 0.19 mmol). Elution with hexane/acetone (4:1) gave light-yellow **12c**. Yield: 76 mg, 64%. Mp: 124 °C. IR (Nujol): ν(CO) 1658 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 7−6.5 (m, 4 × C$_6$*H$_4$*Me-4, 16H), 6.58 (t, $^4J_{HH}$ = 1.5 Hz, *H*C$_6$, 1H), 4.06 (d, C*H$_2$*-aryl, 2H), 3.84 (s, *Me*O, 3H), 3.49 (s, *Me*O, 3H), 3.33 (q, ^3J = 7 Hz, *CH$_2$*Me, 2H), 2.22 (s, *Me* C$_6$H$_4$, 6H), 2.27 (s, *Me* C$_6$H$_4$, 6H), 1.15 (t, *Me*CH$_2$, 3H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, ppm): 184.5 (C=O), 160.5, 153.3, 151.8, 147.8, 142.0, 140.6, 136.9, 136.7, 132.1, 131.2, 129.7 (*C*H), 128.71 (*C*H), 128.66 (*C*H), 128.57 (*C*H), 127.1 (*C*H), 69.6 (*C* spiro), 67.2 (*C*H$_2$), 66.8 (*C*H$_2$), 60.8 (*Me*O), 60.2 (*Me*O), 21.3 (*Me*-C$_6$H$_4$), 21.1 (*Me*-C$_6$H$_4$), 15.1 (*Me*CH$_2$). Anal. Calc for $C_{43}H_{42}O_4$: C, 82.93; H, 6.80. Found: C, 82.74; H, 7.04. Mass spectrum: *m*/*z* (% abundance) 623 (M$^+$ + 1, 15), 622 (M$^+$, 29) 195 (31), 149 (27), 121 (15), 119 (100), 115 (11), 105 (26), 92 (10), 91 (41), 59 (22). Single crystals of **12c** were obtained by cooling saturated solutions of **12c** in a mixture of diethyl ether and *n*-hexane.

Reaction of 5 with MeO$_2$CC≡CCO$_2$Me. Synthesis of 13. Complex **5** (100 mg, 0.19 mmol), MeO$_2$CC≡CCO$_2$Me (54 mg, 0.38 mmol), and Tl(CF_3SO_3) (67 mg, 0.19 mmol) were mixed in CH_2Cl_2 (6 cm^3) and stirred for 1 h. The suspension was filtered over Celite, the filtrate concentrated, and diethyl ether added giving a precipitate of yellow **13**. Yield: 134 mg, 76%. Mp: 183 °C. IR (Nujol): ν(CO) 1720 (s, br), 1700 (s, br) cm^{-1}. Λ_M (acetone): 124 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 9.5−9.4, 8.9−8.7, 7.9−7.0 (m, py, 10H), 6.95 (s, *H*C$_6$, 1H), 4.54, 4.37 (AB system, $^2J_{AB}$ = 13 Hz, C*H$_2$*-aryl, 2H), 4.02 (s, *Me*O, 3H), 3.89 (s, *Me*O, 3H), 3.80 (s, *Me*O, 3H), 3.6−3.4 (m, *CH$_2$*Me, 2H), 3.59 (s, CO$_2$*Me*, 3H), 3.46 (s, CO$_2$*Me*, 3H), 3.25 (s, CO$_2$*Me*, 3H), 3.03 (s, CO$_2$*Me*, 3H), 1.23 ("t", ^3J = 7 Hz, *Me*CH$_2$, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): 170.7 (C=O), 168.9 (C=O), 166.2 (C=O), 160.4 (C=O), 155.2, 154.2 (*C*H-py), 152.9 (*C*H-py), 152.8, 138.7, 138.5 (*C*H-py), 138.4 (*C*H-py), 137.5, 134.6, 124.6 (*C*H-py), 124.5 (*C*H-py), 121.7, 120.4, 117.5, 105.7 (*C*H-aryl), 69.1 (*C*H$_2$), 66.0 (*C*H$_2$), 60.3 (*Me*O), 59.2 (*Me*O), 56.0 (*Me*O), 52.6 (CO$_2$*Me*), 52.2 (CO$_2$*Me*), 52.0 (CO$_2$*Me*), 51.7 (CO$_2$*Me*), 15.2 (*Me*CH$_2$). Anal. Calc for $C_{35}H_{39}N_2F_3O_{15}PdS$: C, 45.54; H, 4.26; N, 3.03; S, 3.47. Found: C, 45.52; H,

Table 1. Specific Crystallographic Details for Compounds 6, 11, 12c, and 13

	compound			
	6	**11**	**12c**	**13**
formula	$C_{40}H_{40}ClN_2O_8PPd$	$C_{25}H_{39}F_3N_2O_{11}PdS$	$C_{43}H_{42}O_4$	$C_{35}H_{39}F_3N_2O_{15}PdS$
M_r	849.56	739.04	622.77	923.14
cryst. habit	yellow tablet	yellow tablet	colorless prism	colorless tablet
cryst size/mm	0.45 × 0.35 × 0.3	0.6 × 0.6 × 0.2	0.58 × 0.36 × 0.18	0.38 × 0.36 × 0.12
system	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_1$	$C2/c$	$P2_12_12_1$
cell consts				
a/Å	13.2936(14)	11.093(5)	36.542(4)	10.132(2)
b/Å	13.5928(12)	11.069(5)	10.4546(14)	19.078(3)
c/Å	20.949(2)	12.679(6)	18.341(2)	20.198(3)
β/deg	92.462(8)	90.54(4)	94.764(6)	90
V/Å^3	3782.0	1556.8	6982.8	3904.4
Z	4	2	8	4
D_x/Mg m^{-3}	1.492	1.577	1.185	1.570
μ/mm^{-1}	0.66	0.74	0.075	0.62
F(000)	1744	760	2656	1888
T/K	173	143	173	173
$2\theta_{max}$/deg	50	50	50	50
no. of reflns	8197	4121	6224	6356
unique reflns	6645	3893	6124	6041
R_{int}	0.031	0.028	0.021	0.036
no. of params	482	398	432	518
no. of restraints	407	310	440	456
$wR(F^2)$, all reflns	0.079	0.067	0.086	0.073
$R(F)$, $F > 4\sigma(F)$	0.036	0.027	0.039	0.049
S	0.91	1.08	0.78	0.80
max $\Delta\rho$/e Å^{-3}	0.55	0.46	0.19	0.46
Flack x param		−0.05(2)		−0.04(3)

4.17; N, 3.25; S, 3.39. Single crystals of **13** were obtained by liquid diffusion of *n*-hexane into a solution of **13** in $CDCl_3$.

Reaction of Complex 10 with PPh_3. Synthesis of 14. Complex **10** (100 mg, 0.13 mmol) and PPh_3 (34 mg, 0.13 mmol) were reacted in CH_2Cl_2 for 12 h. Concentration of the solution and addition of diethyl ether resulted in the precipitation of yellow **14**. Yield: 93 mg, 70%. Mp: 184 °C. Λ_M (acetone): 125 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 9.3−6.7 (5 m, bpy, PPh_3, 2 Ph, 33H), 6.68 (s, HC_6, 1H), 4.35, 3.44 (AB system, $^2J_{AB}$ = 10 Hz, CH_2-aryl, 2H), 3.92 (s, *Me*O, 3H), 3.35−3.12 (m, CH_2Me, 2H), 3.20 (s, *Me*O, 3H), 2.72 (s, *Me*O, 3H), 1.13 ("t", ^3J = 7 Hz, *Me*CH$_2$, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): 156−123 (PPh_3, 2Ph, bpy), 108.2 (*C*H-aryl), 75.7 (CH_2), 66.3 (CH_2), 60.0(*Me*O), 58.8 (*Me*O), 56.0 (*Me*O), 15.2 (*Me*CH$_2$). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, ppm): 32.8. Anal. Calc for $C_{54}H_{50}N_2ClO_8PPd$: C, 63.28; H, 4.91; N, 2.73. Found: C, 63.28; H, 5.25; N, 2.81.

Crystal Structure Analyses. *Crystal data* are presented in Table 1. *Data collection:* Data for **6**, **12c**, and **13** were collected with Mo Kα radiation on a Siemens P4 diffractometer (**11**; Stoe STADI-4) equipped with an LT-2 low-temperature device. Scan type ω was used (**11**; ω/θ). Cell constants were refined from setting angles of ca. 60 reflections in the 2θ range 10−25° (**11**; $\pm\omega$ angles, 2θ 20−23°). *Structure solution:* Direct methods (**12c**, **13**) or heavy-atom method (**6**, **11**). *Structure refinement*: Anisotropic refinement on F^2,[12] H atoms as rigid methyls or with a riding model, weighting schemes $w^{-1} = 2(F^2) + (aP)^2 + bP$, where $3P = (2F_c^2 + F_o^2)$ and a and b are constants optimized by the program. A variety of restraints were applied to light-atom displacement parameters (*DELU*) and aromatic rings (*FLAT*, *SAME*). *Special features of refinement*: For **11** and **13** the absolute structure was determined by an x refinement.[13] For **11** the origin was fixed in terms of a weighted sum of coordinates.[14] For **12** the ethyl group C(51)/(52) was disordered over two sites. Final atomic coordinates are given in Tables 2−5, with selected bond lengths and angles in Tables 6−9.

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(13) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.
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Results and Discussion

Synthesis of the Arylmercury and -palladium Compounds. The reaction of 3,4,5-trimethoxybenzyl chloride with mercury(II) acetate in ethanol results not only in the desired mercuration process but also in the substitution of the chloro atom by an ethoxy group from the solvent. Pouring the alcoholic mixture into aqueous NaCl affords [Hg(Ar)Cl] (**1**) (see Scheme 2). **1** can be symmetrized to [Hg(Ar)$_2$] (**2**) by reacting **1** with (NMe_4)Cl, exploiting the low solubility of the resulting (NMe_4)[$HgCl_3$] (see Scheme 2). Compound **2** reacts with $Na_2[PdCl_4]$ in acetone/water mixtures giving solutions that, after removal of acetone, lead to precipitation of **1** and an aqueous solution containing an arylpalladium complex. A similar behavior was observed with the 6-formylaryl analogue of **2**, where extraction of the aqueous solution with CH_2Cl_2 gave an orthopalladated complex resulting from a rearrangement process.[6] However, in the present case, attempts to extract organopalladium species from the aqueous solution cause decomposition to metallic palladium. Nevertheless, addition to these aqueous solutions of 2,2′-bipyridine (bpy) or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) or pyridine (py), and further extraction with CH_2Cl_2, permit the isolation of the compounds [Pd(Ar)Cl(bpy)] (**3**), [Pd(Ar)Cl(tmeda)] (**4**), or *trans*-[Pd(Ar)Cl(py)$_2$] (**5**), respectively, from the organic layer (Scheme 2). Though the nature of the complex(es) present in these aqueous solutions is unknown, it is clear from our results that they behave as sources of "Pd(Ar)Cl". As far as we are aware, only two palladium complexes containing an ROCH$_2$−aryl ligand have previously been reported.[15]

It is possible to prepare new palladium complexes from **3**−**5**. Thus, the reaction of **3** with PPh_3 and $NaClO_4$ leads to [Pd(Ar)(bpy)(PPh_3)]ClO_4 (**6**), whereas

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Table 2. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for 6[a]

	x	*y*	*z*	*U*(eq)
Pd	7829.8(2)	3285.0(2)	5405.1(1)	22.0(1)
P	6992.1(7)	3014.1(7)	6304.0(4)	25.1(2)
C(1)	7590(3)	1857((2)	5220.4(15)	25.2(8)
C(2)	8268(3)	1171(3)	5486.7(15)	26.4(8)
C(3)	8178(3)	169(3)	5349((2)	27.9(8)
C(4)	7396(3)	−150(3)	4941((2)	31.3(8)
C(5)	6718(3)	517(3)	4670(2)	29.5(8)
C(6)	6813(3)	1517(2)	4806(2)	26.1(8)
O(1)	9004(2)	1481(2)	5925.1(11)	33.5(6)
O(2)	8862(2)	−507(2)	5599.8(12)	36.2(6)
O(3)	7352(2)	−1150(2)	4848.8(13)	43.7(7)
O(4)	5246(2)	1772(2)	4220.0(13)	46.3(7)
C(7)	9995(3)	1478(3)	5675(2)	49.2(12)
C(8)	8666(3)	−805(3)	6234(2)	47.0(11)
C(9)	6496(3)	−1524(3)	4504(2)	44.3(10)
C(10)	6082(3)	2253(3)	4509(2)	37.9(9)
C(01)	4507(3)	2433(4)	3941(2)	58.0(12)
C(02)	4815(4)	2844(4)	3316(2)	80(2)
N(1)	8545(2)	3524(2)	4541.8(12)	23.8(6)
C(11)	8753(3)	2828(3)	4115(2)	29.7(8)
C(12)	9226(3)	3035(3)	3555(2)	31.2(9)
C(13)	9487(3)	3990(3)	3435(2)	35.1(9)
C(14)	9274(3)	4711(3)	3869(2)	30.2(8)
C(15)	8801(2)	4466(2)	4421.2(14)	21.5(7)
C(16)	8542(2)	5198(3)	4913.4(15)	22.8(7)
C(17)	8667(3)	6196(3)	4825(2)	30.7(8)
C(18)	8445(3)	6853(3)	5307(2)	35.8(9)
C(19)	8104(3)	6477(3)	5871(2)	31.1(9)
C(20)	7974(3)	5477(3)	5923(2)	28.8(8)
N(2)	8173(2)	4830(2)	5454.2(12)	22.4(6)
C(21)	7614(3)	3650(3)	6973(2)	30.8(8)
C(22)	7096(3)	4160(3)	7424(2)	44.5(10)
C(23)	7615(4)	4661(3)	7914(2)	57.3(12)
C(24)	8656(4)	4651(3)	7949(2)	53.4(12)
C(25)	9181(3)	4130(3)	7512(2)	39.2(9)
C(26)	8660(3)	3631(3)	7023(2)	32.5(9)
C(31)	6780(3)	1778(3)	6602.2(15)	28.4(8)
C(32)	7291(3)	1429(3)	7143(2)	35.1(9)
C(33)	7111(3)	486(3)	7355(2)	45.7(11)
C(34)	6431(3)	−111(3)	7038(2)	46.8(11)
C(35)	5918(3)	219(3)	6497(2)	41.6(10)
C(36)	6093(3)	1162(3)	6278(2)	34.5(9)
C(41)	5731(3)	3546(3)	6232(2)	29.1(8)
C(42)	5563(3)	4360(3)	5845(2)	38.0(9)
C(43)	4625(3)	4802(3)	5798(2)	48.4(11)
C(44)	3851(3)	4435(4)	6133(2)	52.9(12)
C(45)	3994(3)	3623(3)	6517(2)	51.1(12)
C(46)	4938(3)	3183(3)	6575(2)	39.6(9)
Cl	8356.0(8)	7537.0(7)	7795.5(4)	39.6(2)
O(5)	8552(3)	8503(3)	8018(2)	103.2(15)
O(6)	7624(3)	7571(3)	7297.2(15)	91.3(13)
O(7)	7975(3)	6997(3)	8308(2)	91.5(13)
O(8)	9260(2)	7093(2)	7600(2)	75.7(11)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for 11[a]

	x	*y*	*z*	*U*(eq)
Pd	7905.0(2)	5002.0(3)	7759.5(2)	19.3(1)
C(1)	6291(3)	4798(4)	7052(3)	20.9(10)
C(2)	5469(3)	5650(4)	7272(3)	20.0(8)
C(3)	5745(3)	6559(4)	8110(3)	20.5(8)
C(4)	5773(3)	7789(4)	7878(3)	20.7(8)
C(5)	6136(3)	8629(4)	8621(3)	25.1(8)
C(6)	6419(3)	8257(4)	9653(3)	22.9(8)
C(7)	6331(3)	7048(4)	9903(3)	23.9(8)
C(8)	6023(3)	6198(4)	9144(3)	20.5(8)
C(9)	6009(3)	4886(5)	9444(2)	21.5(8)
C(10)	6017(3)	3734(4)	6376(3)	26.1(9)
C(11)	4690(6)	2083(6)	6152(5)	60(2)
C(12)	4255(3)	5735(4)	6775(3)	23.3(9)
C(13)	3027(4)	5148(8)	5323(4)	56(2)
C(14)	4415(4)	8875(4)	6786(4)	36.5(11)
C(15)	7331(4)	10161(5)	7906(3)	39.6(12)
C(16)	7076(4)	8735(5)	11386(3)	33.2(10)
C(17)	7144(4)	3025(4)	9216(3)	26.5(9)
C(18)	7066(4)	2564(4)	10321(3)	33.0(10)
C(19)	10423(3)	5723(5)	7695(3)	33.0(11)
C(20)	9779(4)	6344(5)	6784(3)	33.5(10)
C(21)	10017(3)	4590(4)	9288(3)	30.7(10)
C(22)	9319(4)	6642(5)	9152(3)	35.0(10)
C(23)	7973(4)	6358(5)	5697(3)	35.1(10)
C(24)	9199(4)	4545(5)	5793(3)	32.8(10)
N(1)	9540(3)	5513(4)	8548(2)	25.3(7)
N(2)	8749(3)	5588(4)	6410(2)	25.7(7)
O(1)	7175(2)	4347(3)	9163(2)	19.7(6)
O(2)	5124(3)	3066(3)	6796(2)	35.9(7)
O(3)	6525(3)	3476(4)	5580(2)	40.3(8)
O(4)	4218(2)	5227(3)	5818(2)	33.6(9)
O(5)	3392(2)	6189(3)	7188(2)	31.2(7)
O(6)	5510(2)	8145(3)	6867(2)	27.0(6)
O(7)	6209(2)	9845(3)	8375(2)	31.7(7)
O(8)	6781(2)	9130(3)	10334(2)	29.0(7)
S	9660.2(9)	6541.9(12)	2815.2(8)	33.8(3)
O(97)	10471(3)	6132(4)	3626(3)	47.9(9)
O(98)	8750(3)	7378(4)	3159(3)	48.9(9)
O(99)	10202(3)	6832(4)	1831(3)	52.1(10)
C(99)	8809(4)	5183(6)	2500(3)	40.7(13)
F(1)	8212(3)	4771(4)	3332(2)	63.6(11)
F(2)	7984(3)	5391(3)	1741(2)	59.0(9)
F(3)	9506(3)	4301(3)	2150(3)	67.3(10)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized $\mathbf{U}ij$ tensor.

reaction of **5** with $AgClO_4$ in acetone results in the elimination of the chloro ligand as AgCl and the presumable formation of the cation $[Pd(Ar)(acetone)(py)_2]^+$. Filtration of the AgCl and addition of pyridine afford $[Pd(Ar)(py)_3]ClO_4$ (**7**). The latter reacts at room temperature with PPh_3 to give a mixture of *cis*- and *trans*-$[Pd(Ar)(PPh_3)(py)_2]ClO_4$. If this mixture is refluxed in acetone only, the *cis* isomer is isolated. The formation of the *trans* isomer must be due to the greater *trans*-effect exerted by the Ar ligand, while its transformation into the *cis* compound can be explained by the *antisymbiotic* effect, according to which PPh_3 *trans* to an aryl ligand is unfavorable.[16] On heating the process is thermodynamically controlled, giving *cis*-$[Pd(Ar)(PPh_3)(py)_2]ClO_4$ (**8**).

Reactions of 3−5 with Alkynes. We have carried out a study of the reactions of these three palladium complexes with various alkynes, in order to determine the influence of the nature of the ligands attached to the metal and of the alkynes. The alkynes used were EtC≡CEt, PhC≡CPh, 4-MeC_6H_4C≡CC_6H_4Me-4, and MeO_2CC≡CCO_2Me, and the positive results are depicted in Schemes 3 and 4. The reactions not represented gave complex mixtures that we could not separate. The reactions were carried out in the presence of $AgClO_4$ or $Tl(CF_3SO_3)$ in order to remove the chloro ligand and thus creating a coordinative vacancy; otherwise untractable mixtures were obtained.

The bpy complex **3** gives clear results only with EtC≡CEt and PhC≡CPh (see Scheme 3). The former gives rise to the π-allyl complex **9** whereas the latter gives the monoinserted palladium complex **10** (see Scheme 3). A similar result is obtained in the reaction

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Table 4. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for 12c[a]

	x	*y*	*z*	*U*(eq)
O(1)	6839.8(4)	4617.0(13)	5664.3(7)	37.7(4)
O(2)	7117.0(4)	7162.0(14)	5536.4(8)	40.9(4)
O(3)	6709.6(4)	9060.5(13)	6081.3(8)	43.3(4)
O(4)	5628.1(4)	7256.2(14)	7235.7(8)	47.3(4)
C(1)	6361.4(5)	5337(2)	6359.7(10)	23.7(4)
C(2)	6104.4(5)	4334(2)	5984.8(10)	24.6(5)
C(3)	6125.3(5)	3247(2)	6383.7(10)	25.6(5)
C(4)	6382.3(5)	3417(2)	7041.7(10)	24.3(5)
C(5)	6526.7(5)	4613(2)	7044.6(10)	23.2(5)
C(6)	6678.2(5)	5676(2)	5921.7(10)	24.7(5)
C(7)	6802.1(5)	6876(2)	5865.6(10)	26.8(5)
C(8)	6597.2(5)	7960(2)	6133.6(10)	29.1(5)
C(9)	6256.1(5)	7679(2)	6455.9(10)	27.9(5)
C(10)	6144.5(5)	6488(2)	6577.3(10)	25.7(5)
C(11)	6965.2(7)	4640(2)	4945.6(12)	54.6(7)
C(12)	7446.7(6)	6875(3)	5978.9(13)	57.6(7)
C(13)	5793.0(6)	6199(2)	6921.8(12)	38.2(6)
C(14)	5767.4(8)	7523(2)	7957.2(13)	61.3(8)
C(15)	5556.4(9)	8592(3)	8258(2)	95(1)
C(21)	5863.5(5)	4655(2)	5320.6(10)	26.8(5)
C(22)	5946.1(6)	5679(2)	4878.4(11)	38.1(6)
C(23)	5718.7(6)	6011(2)	4264.7(11)	40.9(6)
C(24)	5401.0(6)	5346(2)	4069.5(11)	36.3(5)
C(25)	5315.7(6)	4334(2)	4511.4(12)	40.9(6)
C(26)	5539.0(6)	3995(2)	5123.5(11)	34.6(5)
C(27)	5154.8(7)	5707(3)	3397.7(12)	61.0(8)
C(31)	5924.9(5)	2036(2)	6193.1(11)	26.6(5)
C(32)	5999.7(6)	1373(2)	5568.3(11)	35.7(5)
C(33)	5804.4(6)	282(2)	5361.0(12)	41.5(6)
C(34)	5528.3(6)	−174(2)	5755.4(13)	38.5(6)
C(35)	5457.7(6)	478(2)	6383.9(13)	44.0(6)
C(36)	5655.5(6)	1564(2)	6607.0(11)	35.6(5)
C(37)	5313.3(7)	−1356(2)	5516.4(15)	59.4(8)
C(41)	6462.3(5)	2428(2)	7614.5(10)	24.1(5)
C(42)	6526.1(5)	1155(2)	7441.9(11)	28.8(5)
C(43)	6607.3(6)	265(2)	7985.8(11)	33.5(5)
C(44)	6625.6(6)	596(2)	8720.5(11)	32.1(5)
C(45)	6559.0(6)	1866(2)	8889.8(11)	34.0(5)
C(46)	6479.2(5)	2769(2)	8348.6(11)	29.9(5)
C(47)	6722.2(6)	−372(2)	9314.0(11)	46.5(6)
C(51)	6836.2(5)	5148(2)	7518.5(10)	24.8(5)
C(52)	7165.0(6)	4487(2)	7632.3(12)	39.9(6)
C(53)	7462.0(6)	4983(2)	8062.8(12)	42.4(6)
C(54)	7444.0(5)	6166(2)	8389.1(10)	27.8(5)
C(55)	7122.0(6)	6836(2)	8261.9(11)	36.8(6)
C(56)	6822.7(6)	6348(2)	7838.9(11)	35.8(6)
C(57)	7759.9(6)	6697(2)	8873.7(11)	39.3(6)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized **U***ij* tensor.

Table 5. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for 13[a]

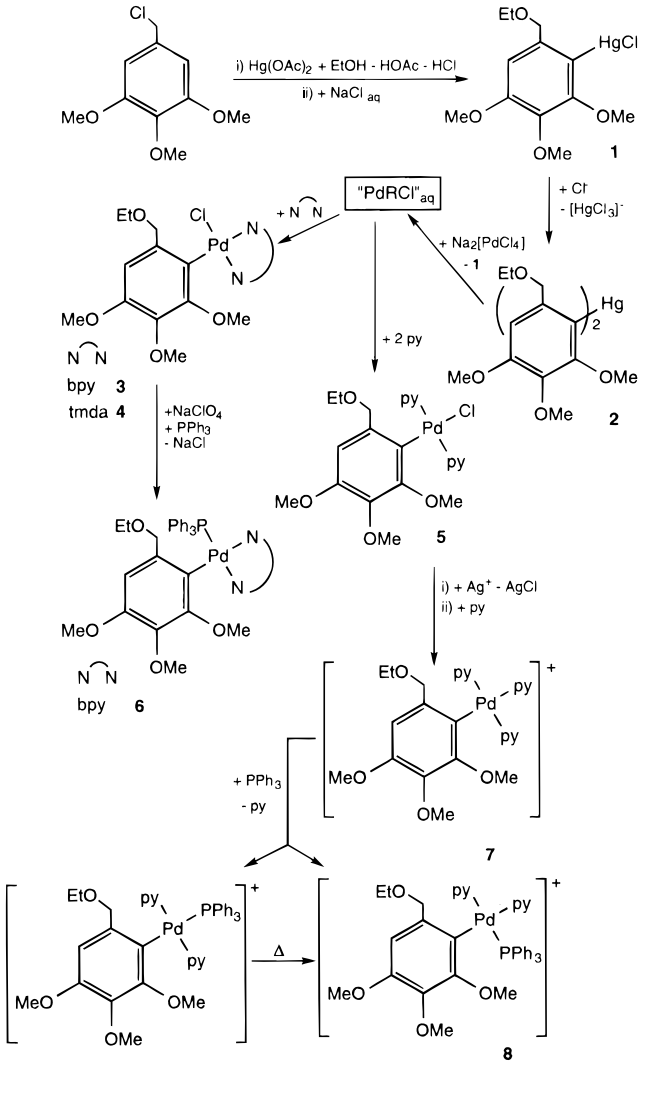
	x	*y*	*z*	*U*(eq)
Pd	6745.0(6)	−260.1(3)	3332.8(3)	23.9(1)
S	8994(2)	−1158.8(12)	4178.9(12)	41.6(6)
O(1)	5784(4)	−506(2)	1739(3)	39.0(13)
O(2)	3954(5)	−406(2)	2361(2)	33.0(13)
O(3)	5074(5)	1950(2)	1929(2)	44(2)
O(4)	4293(5)	893(2)	1670(3)	45.0(14)
O(5)	7862(5)	2498(2)	2806(2)	44(2)
O(6)	7997(6)	1594(2)	2099(2)	37.9(14)
O(7)	6747(6)	2618(2)	4302(3)	46.7(14)
O(8)	8473(5)	1949(3)	4050(2)	35.7(14)
O(9)	7700(5)	−861(3)	4093(2)	39(2)
O(10)	9808(6)	−756(3)	4635(3)	72(2)
O(11)	9623(6)	−1387(3)	3608(3)	82(2)
O(12)	6998(5)	711(2)	4668(2)	40.6(14)
O(13)	5119(5)	188(3)	5586(2)	48.8(15)
O(14)	2576(5)	509(3)	5420(2)	41(2)
C(1)	5777(6)	284(4)	2658(3)	23(2)
C(2)	5169(7)	−238(4)	2186(3)	24.0(15)
C(3)	3372(9)	−1009(3)	2055(3)	51(2)
C(4)	5742(7)	972(3)	2581(3)	23(2)
C(5)	5038(7)	1324(4)	2035(4)	28(2)
C(6)	3572(7)	1187(4)	1139(3)	48(2)
C(7)	6536(8)	1481(4)	3006(4)	25(2)
C(8)	7516(7)	1933(4)	2640(4)	29(2)
C(9)	8907(6)	1992(3)	1702(4)	44(2)
C(10)	6383(7)	1587(4)	3654(4)	25(2)
C(11)	7216(8)	2113(4)	4024(4)	33(2)
C(12)	9318(8)	2434(4)	4412(4)	63(3)
C(13)	8647(10)	−1934(5)	4652(6)	61(3)
N(2)	8454(6)	113(2)	2980(2)	21.0(13)
C(21)	8907(6)	−74(3)	2386(3)	28(2)
C(22)	10150(7)	96(4)	2173(3)	37(2)
C(23)	10996(8)	472(4)	2569(4)	39(2)
C(24)	10520(7)	677(4)	3173(4)	39(2)
C(25)	9272(6)	488(3)	3371(4)	28(2)
N(1)	5033(6)	−715(3)	3645(3)	25.1(15)
C(31)	3945(7)	−373(4)	3798(3)	28(2)
C(32)	2802(7)	−690(4)	4010(4)	40(2)
C(33)	2801(7)	−1403(4)	4068(4)	44(2)
C(34)	3898(8)	−1778(4)	3910(4)	41(2)
C(35)	5005(7)	−1422(4)	3699(3)	32(2)
C(41)	5333(7)	1295(4)	4085(3)	24(2)
C(42)	5688(7)	877(4)	4627(4)	27(2)
C(43)	4733(8)	617(4)	5060(3)	31(2)
C(44)	3437(8)	798(3)	4984(3)	31(2)
C(45)	3074(7)	1245(3)	4471(3)	24(2)
C(46)	4006(8)	1486(4)	4024(3)	25(2)
C(47)	7662(8)	851(5)	5293(4)	70(3)
C(48)	5465(10)	−520(4)	5400(4)	84(4)
C(49)	1213(7)	658(4)	5327(4)	47(2)
C(50)	3594(7)	1991(4)	3488(4)	45(2)
O(15)	2312(5)	2206(3)	3551(3)	68(2)
C(51)	1739(17)	2482(7)	2926(6)	61(4)
C(52)	2218(19)	3080(9)	2755(10)	122(7)
C(51′)	2073(24)	2871(12)	3127(13)	61(4)
C(52′)	890(25)	3114(13)	3164(16)	122(7)
F(1)	9738(6)	−2293(2)	4778(3)	85(2)
F(2)	8046(7)	−1797(3)	5202(3)	124(3)
F(3)	7897(8)	−2360(3)	4292(4)	165(4)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

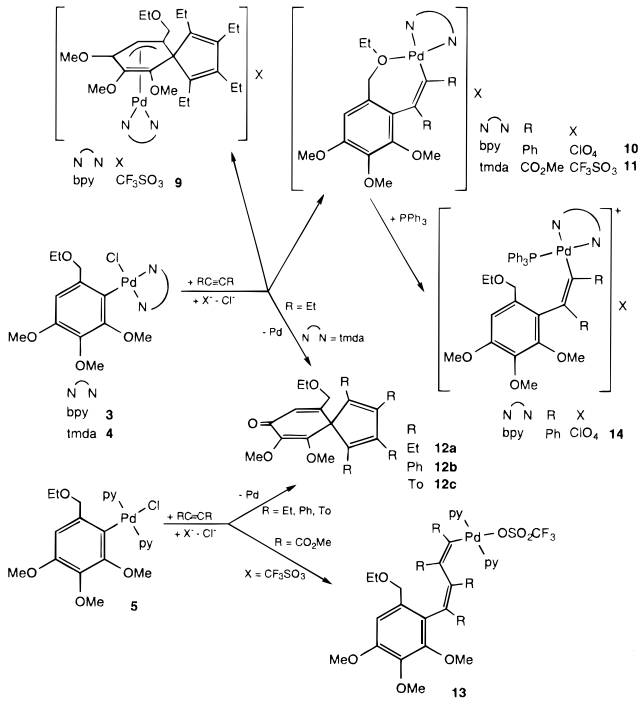
of the tmeda complex **4** and $MeO_2CC{\equiv}CCO_2Me$, giving **11**. A depalladation process, giving the organic spirocyclic compound **12a**, is observed when **4** or **5** react with $EtC{\equiv}CEt$ (**12a**) (molar ratio ≤ 1:2). Related compounds are obtained by reacting **5** with diarylacetylenes $RC{\equiv}CR$, R = Ph (**12b**) and To (C_6H_4Me-4) (**12c**). The alkyne $MeO_2CC{\equiv}CCO_2Me$ reacts differently with **5**, giving a monoinserted complex when the molar ratio is 1:1 or the diinserted complex **13** when this ratio is ≥2:1. The monoinserted complex could not be obtained analytically pure, but its ^1H and ^{13}C NMR spectra clearly show the presence of five MeO groups. Compounds **9**-**12** and **13** were also obtained even when an excess of the alkynes was used.

The reactivity of **3**-**5** with alkynes seems to be erratic. This is also the impression when the complete area of the reactions between arylpalladium complexes and alkynes is observed.[8] However, our results are interconnected because compounds **9**-**11** and **13** can be considered as models for the intermediates in the formation of spirocyclic compounds **12a**-**c**. We have proposed a reaction pathway in the synthesis of similar spiro compounds starting from (6-acetyl-2,3,4-trimethoxyphenyl)palladium complexes.[1] Scheme 4 adapts such a proposal to the synthesis of **12a**-**c** and shows those intermediates that we have isolated. Complexes **10** and **11** constitute models of the intermediate resulting from the initial coordination of one alkyne and its insertion into the arylic carbon−palladium bond (**A** in Scheme 4). The formation of such monoinserted cyclometalated complexes is well documented, although not with oxygen

Scheme 2



Scheme 3



as the heteroatom bonded to palladium.[8c,d,k,o] It is also noteworthy that, whereas complexes **10** and **11** are stable cyclometalated species with seven-membered rings, it was not possible to isolate the supposedly more favorable five-membered ring complexes with the Ar group, since all our attempts to coordinate this oxygen atom, for example, by reacting **3**-**5** with $TlCF_3SO_3$, led to ill-defined complexes. It is probable that coordination of the oxygen atom is prevented because of the repulsion between the *ortho* MeO group and the *cis* ligand. As far as we are aware, only one paper reports reactions of palladacycles stabilized by an O → Pd bond with an alkyne. However, in all cases monoinserted complexes were obtained.[17]

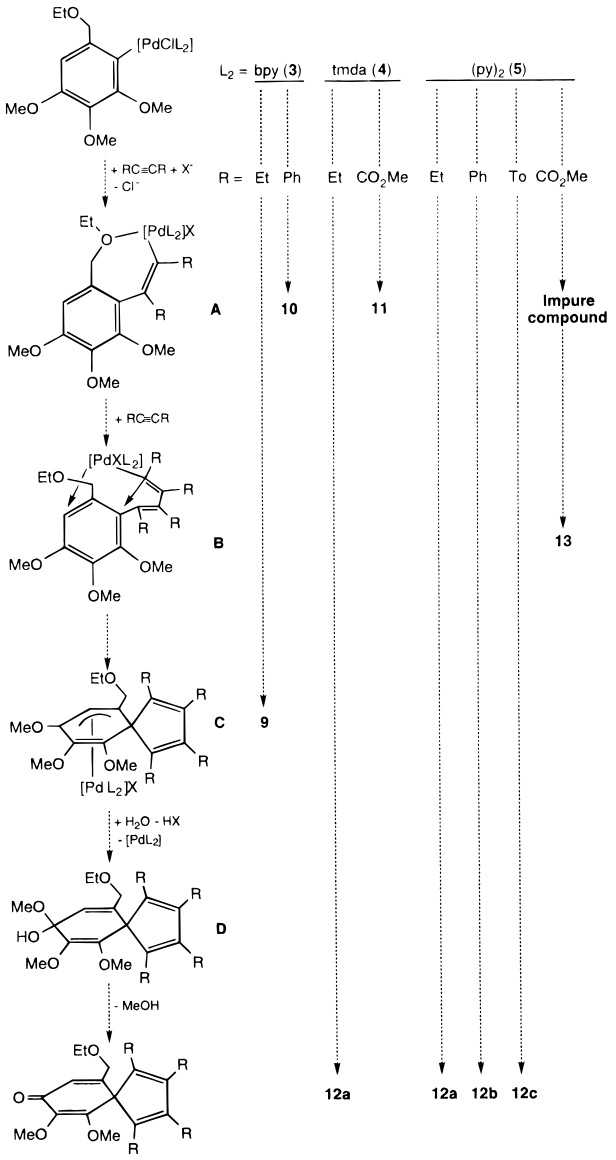
The second step consists of the insertion of a second alkyne to give a butadienyl derivative (**B** in Scheme 4). Complexes of this type have previously been isolated by the reaction of orthometalated palladium complexes, Ar−[Pd], with alkynes R_2C_2. However, their structures invariably show a [Pd]−*cis*-CR═CR-*trans*-CR═CR(Ar) chain with an additional bond between the metal center and the *trans*-C═C-π electron system (see **D** in Scheme 5). In addition, a third bond is established between a donor atom (N or S) of some substituent of the Ar group and the palladium atom.[8] This process requires that the first alkyne inserted should change from the original *cis* to *trans* geometry. Two different mechanisms have been proposed for this isomerization. In the first (see **A** → **B** → **C** → **D** in Scheme 5),[8c] the second alkyne insertion is also cis (see **B** in Scheme 5), but a *cis* to *trans* isomerization takes place to give the final isolated complex (see **D** in Scheme 4). The assumption of an equilibrium **B** ⇌ **C** ⇌ **D** is based on the observation that some derivatives of these intermediates have a *cis*,*cis* geometry.[8q] The second proposal (**A** → **B′** → **C′** → **D**)[8j] assumes that the second insertion leads to a palladacyclobutene intermediate (**C′**) that, after cleavage of the first η^1-alkene−Pd σ bond, gives finally the *cis*,*trans*-butadienylpalladium complex. Our complex **13** is the first example of a *cis*,*cis* di-insertion of an alkyne into an arylpalladium bond, confirmed by its crystal structure (see below). Its isolation could be interpreted as support for the first mechanistic proposal. However, it is also possible that, in our case, no *cis* to *trans* isomerization occurs because the driving force for such isomerization is probably the E → Pd bond and, in our case, the O → Pd could not exist (as in **13**). In fact, a *cis*,*cis* double insertion of alkynes into a Pd−Cl bond is observed when starting from $[PdCl_2(NCPh)_2]$.[18] The isolation of **13** and not the corresponding intermediates (**B** in Scheme 4) in the synthesis of **9** or **12a**-**c** could be due to the greater stability of the *cis*-CR═CR-*cis*-CR═CR(Ar) σ bond with Pd when R = CO_2Me. Thus, when L = py and R = Ph, Et or L_2 = tmda and R= Et, the organic spiro compounds **12a**-**c** are obtained without isolation of any intermediate. In contrast, intermediates **11**, **13**, and the monoinserted precursor of **13** are obtained when R = CO_2Me. The ligand bpy also confers special stability on intermediates and thus, for example, no spontaneous depalladation is observed from **3,** intermediates **9** and **10** being isolated instead.

The third step may be ring contraction of the diinserted species **B** to give a (π-allyl) palladium complex

(17) Ossor, H.; Pfeffer, M.; Jastrzebski, J. T. B. H.; Stam, C. H. *Inorg. Chem.* **1987**, *26*, 1169.

(18) Maitlis, P. M. *J. Organomet. Chem.* **1980**, *200*, 161.

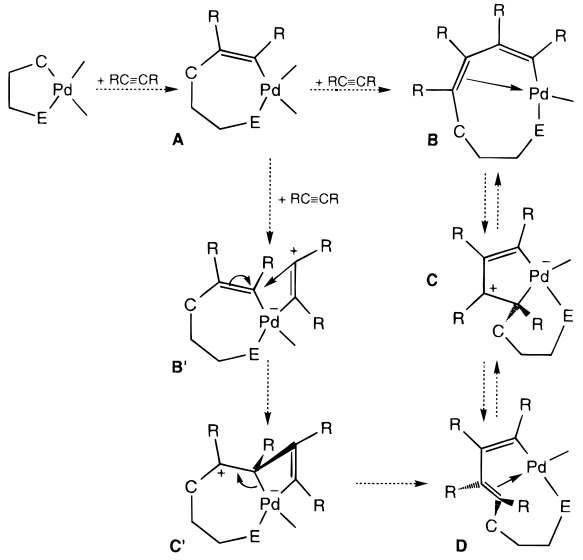
Scheme 4



containing the spiro framework (see **C** in Scheme 4), such as the isolated complex **9**. The C−C bond formation is facilitated by the relatively short distance between both atoms (see below). The reaction between [Pd{C_6H\{C(O)Me\}-(-6-(OMe)$_3$-2,3,4}(μ-Cl)]$_2$ and diarylacetylenes was assumed to proceed through a similar complex [Pd(η^3-allyl)(μ-Cl)]$_2$.[1] We isolated the reaction product of this intermediate with thallium triflate and bpy, and its crystal structure revealed a species of a nature similar to that proposed for **9** (see below). A similar intermediate from reaction of diphenylacetylene and orthopalladated 2-benzylpyridine has been isolated.[8q]

We have proposed that formation of the keto group and depalladation occur through reaction of **C** with adventitious water, leading to intermediate **D** (see Scheme 4) because using freshly distilled solvent, slow decomposition is initially observed but rapidly stops. The resulting solution remains unaltered, but addition of water gives the spiro compound.[1] We assume that the same pathway is operative in the synthesis of compounds **12a**−**c**. The behavior of EtC≡CEt toward complexes **3**−**5** is different from that observed with the related (6-acetyl-trimethoxyphenyl)palladium complex

Scheme 5. Proposed Mechanisms for the Second Insertion of an Alkyne into a Cyclometalated Palladium Complex (E = Nitrogen or Sulfur Donor Moiety)



because only the product of the monoinsertion reaction was obtained (see Scheme 1).[1]

We have unsuccessfully attempted to depalladate complex **10** by treating it with PPh_3, but even on heating, the compound [Pd{*cis*-CPh=CPh(Ar)}(PPh_3)(bpy)]ClO_4 (**14**) (see Scheme 3) was isolated.

NMR Spectra. As expected, the mercurials **1** and **2** and the palladium complexes **5** and **7** show a singlet at 4.4−5.0 ppm in their ^{1}H NMR spectra assignable to the benzyl CH_2 protons. However, these protons appear as an AB system in complexes **3**, **4**, **6**, **8**, and **14** because rotation about the aryl carbon−palladium bond is restricted at room temperature on the NMR time scale. The same behavior has been noted previously.[15] Such a restriction is also responsible for the observation of four singlets corresponding to the methyl groups of the ligand tmda in complex **4**, both in their ^{1}H and ^{13}C NMR spectra.

The monoinserted complexes **10** and **11** also show the presence of an AB system for the benzylic CH_2 protons in the ^{1}H NMR spectra. This is the expected system for such protons, the oxygen atom being rendered chiral by its bonding to the palladium atom. If inversion, on the NMR time scale, of the chirality around the oxygen atom is assumed, the puckering of the ring could give account for the diastereotopic nature of the CH_2 protons. Accordingly, the Me groups of the tmeda ligand in **11** appear as four signals in the ^{1}H and ^{13}C NMR spectra. Compound **13** in solution must retain the nonplanar configuration observed in the solid state (see below) because the benzylic CH_2 protons also appear as an AB system in its ^{1}H NMR spectrum. However, in these compounds with diasterotopic methylene protons, the resonances corresponding to the Et protons have a deceptively simple appearance because, instead of those resonances expected for an ABX_3 system, a quartet and a triplet are observed for the CH_2 and Me protons, respectively.

X-ray Structural Studies. Compounds **6**, **11**, **12c**, and **13** have been studied by X-ray diffraction. The cation of complex **6** (see Figure 1 and Tables 2 and 6)

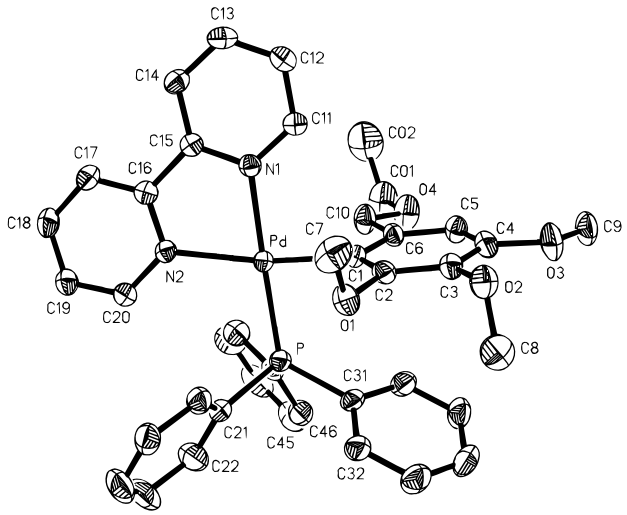


Figure 1.

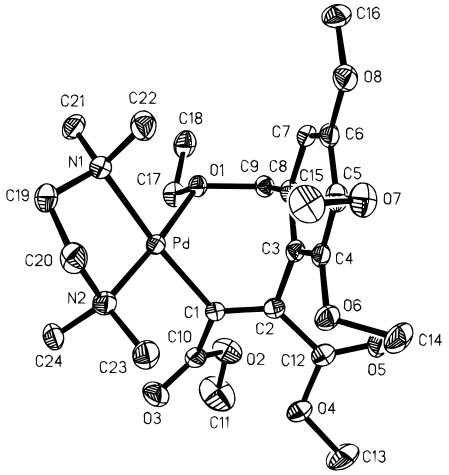


Figure 2.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for 6

Pd−C(1)	2.002(3)	Pd−P	2.2589(9)
Pd−N(1)	2.104(3)	O(4)−C(10)	1.404(4)
Pd−N(2)	2.151(3)	O(4)−C(01)	1.436(5)
C(1)−Pd−N(1)	93.32(11)	N(2)−Pd−P	103.33(7)
N(1)−Pd−N(2)	77.73(10)	C(10)−O(4)−C(01)	113.6(3)
C(1)−Pd−P	85.57(9)		

shows a distorted square-planar coordination (mean deviation of 5 atoms 0.02 Å) of the ligands bpy, Ar, and PPh_3 around the metal center. The maximum distortions correspond to the N(1)−Pd−N(2) [77.73(10)°] (narrow bite of the bpy ligand) and N(2)−Pd−P [103.33(7)°] angles, respectively. The aryl ligand (with its immediate substituents) is almost planar (mean deviation 0.02 Å) and perpendicular (82°) to the coordination plane. The greater *trans* influence of aryl group with respect to PPh_3 causes Pd−N(2) [2.151(3) Å] to be longer than Pd−N(1) [2.104(3) Å]. The Pd−C(1) [2.002(3) Å] and Pd−P [2.151(3) Å] bond distances are normal.[19] There is a short contact of 3.08 Å between the palladium atom and the perchlorate oxygen O(1).

The cation of **11** (see Figure 2 and Tables 3 and 7) shows a puckered seven-membered metallacycle formed by the monoinserted alkyne and the aryl moiety connected to the palladium atom through the oxygen O(1) of the ethoxide group. The coordination deviates significantly from planar; the angle between the planes Pd,C(1),N(2),O(1)/Pd,N(1),N(2),O(1) is 11°. Here too the carbon donor atom has the greater *trans* influence as shown by the longer Pd−N(1) bond distance [2.139(3) Å] than Pd−N(2) [2.063(3) Å]. Coordination to palladium of the oxygen atom of the ethoxide group leads to a slight increase of both C−O bonds [1.466(5), 1.470(4) Å] and a decrease of the C−O−C bond angle [111.9(3)°] with respect to the corresponding values in complex **6** [1.436(5), 1.404(4) Å, 113.6(3)°].

The structure of **12c** (see Figure 3 and Tables 4 and 8) consists of two ring systems, 2,3,4,5-tetra-*para*-

(19) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

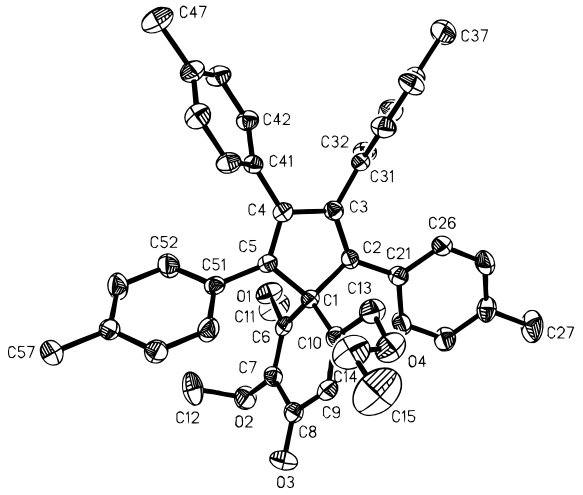


Figure 3.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for 11

Pd−C(1)	2.007(3)	C(8)−C(9)	1.501(7)
Pd−N(2)	2.063(3)	C(9)−O(1)	1.470(4)
Pd−O(1)	2.092(3)	C(17)−O(1)	1.466(5)
Pd−N(1)	2.139(3)	S−O(99)	1.427(3)
C(1)−C(2)	1.343(6)	S−O(97)	1.433(3)
C(2)−C(3)	1.494(5)	S−O(98)	1.440(4)
C(3)−C(4)	1.393(6)	S−C(99)	1.818(6)
C(3)−C(8)	1.402(5)		
C(1)−Pd−N(2)	94.28(13)	C(4)−C(3)−C(8)	118.1(4)
C(1)−Pd−O(1)	89.43(13)	C(4)−C(3)−C(2)	120.9(3)
N(2)−Pd−N(1)	85.13(13)	C(8)−C(3)−C(2)	121.0(4)
O(1)−Pd−N(1)	91.58(12)	C(7)−C(8)−C(3)	120.4(4)
C(2)−C(1)−C(10)	122.7(3)	C(7)−C(8)−C(9)	118.9(3)
C(2)−C(1)−Pd	115.6(3)	C(3)−C(8)−C(9)	120.7(3)
C(10)−C(1)−Pd	121.6(3)	O(1)−C(9)−C(8)	108.7(3)
C(1)−C(2)−C(12)	124.9(4)	C(17)−O(1)−C(9)	111.9(3)
C(1)−C(2)−C(3)	119.1(3)	C(17)−O(1)−Pd	113.2(2)
C(12)−C(2)−C(3)	116.0(3)	C(9)−O(1)−Pd	114.5(2)

Table 8. Selected Bond Lengths (Å) and Angles (deg) for 12c

O(3)−C(8)	1.228(2)	C(4)−C(5)	1.356(2)
C(1)−C(6)	1.505(3)	C(4)−C(41)	1.486(3)
C(1)−C(10)	1.512(3)	C(5)−C(51)	1.478(3)
C(1)−C(2)	1.532(2)	C(6)−C(7)	1.341(3)
C(1)−C(5)	1.546(2)	C(7)−C(8)	1.465(3)
C(2)−C(3)	1.350(2)	C(8)−C(9)	1.453(3)
C(2)−C(21)	1.481(3)	C(9)−C(10)	1.335(3)
C(3)−C(4)	1.477(3)	C(10)−C(13)	1.508(3)
C(3)−C(31)	1.490(3)		
C(6)−C(1)−C(10)	113.4(2)	C(2)−C(1)−C(5)	102.3(2)
C(6)−C(1)−C(2)	113.1(2)	O(3)−C(8)−C(9)	121.7(2)
C(10)−C(1)−C(2)	110.4(2)	O(3)−C(8)−C(7)	121.0(2)
C(6)−C(1)−C(5)	106.4(2)	C(9)−C(8)−C(7)	117.3(2)
C(10)−C(1)−C(5)	110.7(2)		

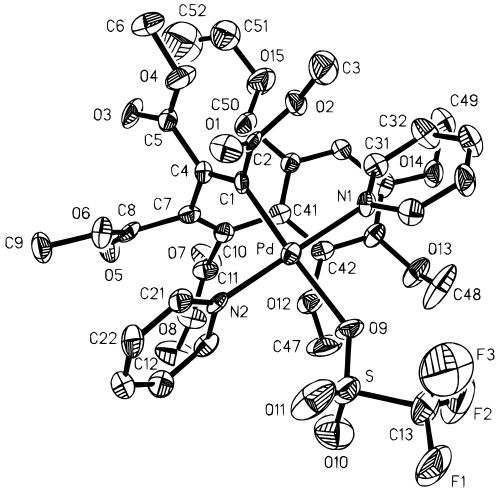
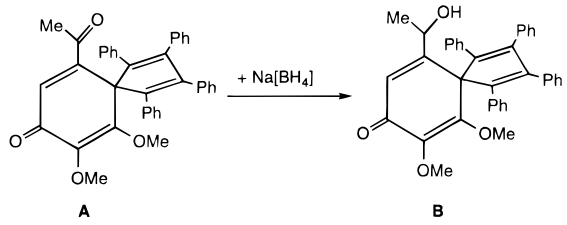


Figure 4.

Scheme 6



tolylcyclopenta-2,4-diene and 2,3-dimethoxy-6-(ethoxymethylene)cyclohexa-2,5-dien-4-one, with a common spiro carbon atom C(1). The bond lengths and angles are similar to those found in the 1-hydroxyethyl derivative (see **B** in Scheme 6), which we prepared[1] from the phenyl derivative (**A** in Scheme 6) related to **12c**.

The structure of **13** (see Figure 4 and Tables 5 and 9) shows a slightly distorted square-planar coordination (mean deviation 0.05 Å) of the ligands around the metal center, the pyridine molecules being mutually *trans*. The butadienyl ligand forms a spiral chain that places the carbon atom initially bonded to palladium, C(41), near the carbon bonded to palladium, C(1) (3.50 Å). This situation could also exist in the intermediates **B** in Scheme 4, thus facilitating the formation of the spiro intermediate **C**.

Table 9. Selected Bond Lengths (Å) and Angles (deg) for 13

Pd−C(1)	1.975(7)	C(1)−C(2)	1.511(9)
Pd−N(2)	2.003(5)	C(4)−C(5)	1.475(9)
Pd−N(1)	2.040(6)	C(4)−C(7)	1.526(9)
Pd−O(9)	2.147(5)	C(7)−C(10)	1.333(8)
S−O(11)	1.388(6)	C(7)−C(8)	1.508(9)
S−O(9)	1.440(5)	C(10)−C(41)	1.483(9)
S−O(10)	1.455(6)	C(10)−C(11)	1.510(9)
C(1)−C(4)	1.321(9)		
C(1)−Pd−N(2)	89.8(2)	C(1)−C(4)−C(7)	123.5(6)
C(1)−Pd−N(1)	90.9(2)	C(5)−C(4)−C(7)	112.7(6)
N(2)−Pd−O(9)	93.1(2)	C(10)−C(7)−C(8)	118.1(7)
N(1)−Pd−O(9)	86.3(2)	C(10)−C(7)−C(4)	125.9(8)
C(4)−C(1)−C(2)	124.8(6)	C(8)−C(7)−C(4)	115.8(6)
C(4)−C(1)−Pd	128.0(5)	C(7)−C(10)−C(41)	127.1(8)
C(2)−C(1)−Pd	106.9(5)	C(7)−C(10)−C(11)	121.4(8)
C(1)−C(4)−C(5)	123.5(7)	C(41)−C(10)−C(11)	111.1(6)

Conclusions. We have shown that $[Hg(Ar)_2]$ (Ar = $C_6H(CH_2OEt)$-6-$(OMe)_3$-2,3,4), obtained from 3,4,5-trimethoxybenzyl chloride and mercury(II) acetate in ethanol, reacts with $K_2[PdCl_4]$ giving water-soluble arylpalladium species from which neutral and cationic complexes can be isolated. By reacting some of these species with alkynes, it is possible to isolate spiro compounds and model complexes of their synthetic intermediates.

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Supporting Information Available: Tables giving crystal data and details of the structure determination, complete atom coordinates and *U* values, bond lengths and angles, and anisotropic displacement coefficients (32 pages). Ordering information is given on any current masthead page.

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