Palladium-Assisted Formation of Carbon−Carbon Bonds. 6.[1] Study of the Reactivity of (*o*-Formylaryl)- or (*o*-Acetylaryl)palladium Complexes with Alkynes. Synthesis of Indenones and Indenols

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The reaction of $(PhCH_2PPh_3)_2[Pd(R^1)Cl(\mu\text{-}Cl)]_2$ (**1**; R^1 = 6-formyl-2,3,4-trimethoxyphenyl) with PhC≡CPh gives a 6.5:1 mixture of 4,5,6-trimethoxy-2,3-diphenylindenone (**2**)and 4,5,6-trimethoxy-2,3-diphenyl-1*H*-indenol (**3**). When the same reaction is carried out with $MeO_2CC{\equiv}CCO_2Me$ or with $Me_3SiC{\equiv}CSiMe_3$, the compounds 4,5,6-trimethoxy-2,3-bis(methoxycarbonyl)indenone (**4**) and $R^1C{\equiv}CSiMe_3$ (**5**) are obtained, respectively. The reactions of PhC≡CPh with $[Pd(R^1)Cl(bpy)]$ (**6**; bpy = 2,2′-bipyridine), in the presence of $AgClO_4$, or with $[Pd(R^1)(MeCN)(bpy)]ClO_4$ (**7**) yield **3** and $[Pd(\mu\text{-}OH)(bpy)]_2(ClO_4)_2$ (**8a**). If **7** reacts with PhC≡CPh under anhydrous conditions, the indenone **2** is obtained. The complex $[Pd(R^2)(MeCN)(bpy)]ClO_4$ (**9**; R^2 = 2-formyl-3,4,5-trimethoxyphenyl) reacts with PhC≡CPh, giving 5,6,7-trimethoxy-2,3-diphenyl-1*H*-indenol (**10**) or, under anhydrous conditions, 5,6,7-trimethoxy-2,3-diphenylindenone (**11**). A 1:1 mixture of both compounds is obtained by reacting $[Pd(\eta^2\text{-}R^2)(\mu\text{-}Cl)]_2$ (**12**) with PhC≡CPh. $[Pd(\eta^2\text{-}R^3)(bpy)](CF_3SO_3)$ (**13**; R^3 = 6-acetyl-2,3,4-trimethoxyphenyl) reacts with the alkynes RC≡CR′ (R = R′ = Ph, 4-tolyl, CO_2Me, Me, Et; R = Ph, R′ = CO_2Et, 4-nitrophenyl, 4-methoxyphenyl, Me; R = ^{t}Bu, R′ = H, Me), yielding $[Pd(\mu\text{-}OH)(bpy)]_2(CF_3SO_3)_2$ (**8b**) and 1-methylindenols **14**−**24**. The catalytic reaction of $[Hg(R^1)_2]$ with PhC≡CPh and $CuCl_2$ in the presence of $Q_2[Pd_2Cl_6]$ (1:6:2:0.05; Q = Me_4N, $PhCH_2PPh_3$) gives the indenol **3** in 62% yield with respect to the group R present in the mercurial compound. When a similar reaction (Q = $PhCH_2PPh_3$) is carried out under nitrogen, the spirocyclic compound 10-formyl-6,7-dimethoxy-1,2,3,4-tetraphenylspiro[4.5]1,3,6,9-decatetraen-8-one (**26**) is obtained.

Introduction

Indenones have been used as fungicides, estrogen binding receptors, and fermentation activators.[2] They are also useful intermediates in the synthesis of a variety of natural products (*e.g.*, steroids or gibberellins).[2a−c] They can be prepared by following traditional organic synthetic methods[3] or by metal-mediated reactions using carbonyl complexes of rhodium,[4] nickel,[5] or iron[6] and alkynes. In these cases, the indenone carbonyl group comes from a coordinated carbon monoxide. Ortho-manganated aryl ketones have been reported to react with alkynes to give indenones or indenols, depending on the substituent attached to the keto group.[7] The metal-catalyzed synthesis of indenones has been achieved by treatment of *o*-alkynyl-substituted α-diazoacetophenone in the presence of rhodium(II) carboxylates,[8] by palladium-catalyzed reactions of alkynes with *o*-diiodobenzene, EtC≡CEt, Zn, and CO,[5] or with *o*-iodo- or *o*-bromobenzaldehyde.[2a,9]

Indenols can be used as intermediates in the synthesis of organic compounds such as indenyl chrysanthemates, which possess insecticidal properties.[10] Some indenols have also shown analgesic and myorelaxation activity.[11] They can be prepared by the reaction of ortho-manganated aryl ketones or benzaldehydes with alkynes.[7,12]

We now report the reaction of (6-formyl-2,3,4-trimethoxyphenyl)-, (2-formyl-3,4,5-trimethoxyphenyl)-, and (6-acetyl-2,3,4-trimethoxyphenyl)palladium complexes

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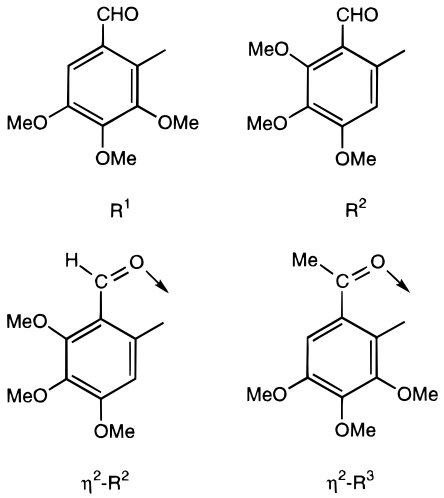
with a variety of symmetrical and unsymmetrical alkynes which result in the formation of indenones and indenols. The trimethoxyaryl grouping is present in organic molecules of pharmaceutical interest: for example, the antileukemic lactones steganacin and steganangin,[13] the antibacterial agent trimethoprim,[14] the cytotoxic colchicine,[15] and the antitumoral agent podophyllotoxin.[16] Some of the results presented here have been published as a preliminary communication.[17]

Experimental Section

C, H, N, and S analyses, melting point measurements, infrared and NMR spectra, NOE studies, and purification of solvents were carried out as described previously.[18] Bis(4-tolyl)acetylene,[19] (4-nitrophenyl)phenylacetylene,[20] and (4-methoxyphenyl)phenylacetylene[21] were prepared following reported procedures. Reactions were carried out at room temperature and without precautions to exclude atmospheric moisture, unless otherwise stated. Chromatographic separations were performed using preparative UV-active silica gel 60 TLC plates (*ca.* 30 × 30 cm) and were visualized with 254 and 365 nm light. Complexes **1**, **6**, **7**, **9**, **12**,[22] **13**, and **25**[23] (see Schemes 1−3) were prepared as previously reported. Chart 1 shows the notation used for the different aryl groups (R^1, R^2, η^2-R^2, η^2-R^3). Relative amounts of regioisomers were determined by comparing the values of the integral of selected signals in the ^{1}H NMR spectra of the reaction mixtures.

Reactions of $(PhCH_2PPh_3)_2[Pd(R^1)Cl(\mu\text{-}Cl)]_2$ (1) with Alkynes. With PhC≡CPh. Complex **1** (36 mg, 0.024 mmol) and PhC≡CPh (44 mg, 0.24 mmol) were mixed in dichloromethane (5 cm^3) and stirred for 72 h. The mixture was filtered over anhydrous $MgSO_4$ and the resultant solution evaporated to dryness. The residue contained (by NMR spectroscopy) compounds **2** and **3** in a molar ratio of 6.5:1. Compound **3** was better prepared from **6** (see below). The above residue was extracted with *n*-hexane and chromatographed on an Al_2O_3 column. Elution with a dichloromethane/hexane mixture (2:1) gave a red solution from which red 4,5,6-trimethoxy-2,3-diphenylindenone (**2**) was obtained. Yield: 14 mg, 77%. Mp: 121−122 °C. IR: ν(C═O) 1700 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 7.35 (m, Ph, 5H), 7.17 (m, Ph, 5H), 7.09 (s, H7, 1H), 3.92 (s, MeO, 3H), 3.88 (s, MeO, 3H), 3.30 (s, MeO, 3H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, ppm): 195.5 (C═O), 156.3, 154.3, 149.4, 147.7, 134.5, 132.3, 130.7, 129.7, 129.0, 128.5, 127.7, 127.3, 126.7, 105.0 (C7), 61.14 (MeO), 61.07 (MeO), 56.55 (MeO). Mass spectrum: *m*/*z* (% abundance) 372 (M$^+$, 71), 215 (100), 213 (39), 178 (24), 113 (40), 108 (38), 107 (46), 95 (36). Anal. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.34; H, 5.48.

Chart 1



With $MeO_2CC{\equiv}CCO_2Me$. Dimethyl acetylenedicarboxylate (37 mg, 0.26 mmol) in acetonitrile (4 cm^3) was slowly added (45 min) to a refluxing acetonitrile (10 cm^3) solution of complex **1** (170 mg, 0.12 mmol). The resulting mixture was refluxed for 1 h, stirred at room temperature overnight, and then evaporated to dryness. The residue was extracted with hot Et_2O. Partial evaporation and cooling of the resulting solution gave red crystals of 4,5,6-trimethoxy-2,3-bis(methoxycarbonyl)indenone (**4**). Yield: 14 mg, 17%. Mp: 162−165 °C. IR: ν(C═O) 1736, 1716, 1693 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 7.02 (s, H7, 1H), 4.01 (s, MeO, 3H), 3.93 (s, MeO, 3H), 3.91 (s, MeO, 3H), 3.89 (s, MeO, 3H), 3.84 (s, MeO, 3H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, ppm): 189.6 (C═O), 165.6 (CO_2Me), 161.4 (CO_2Me), 158.6, 157.8, 149.5, 146.6, 125.7, 124.0, 120.6, 105.6 (C7), 61.7 (MeO), 61.04 (MeO), 56.7 (MeO), 52.8 (MeO), 52.1 (MeO). Mass spectrum: *m*/*z* (% abundance) 336 (M$^+$, 51), 305 (19), 219 (100), 218 (57), 217 (27), 204 (24), 167 (32), 149 (87), 119 (49), 117 (27). Anal. Calcd for $C_{16}H_{16}O_8$: C, 57.14; H, 4.80. Found: C, 57.12; H, 4.73.

With $Me_3SiC{\equiv}CSiMe_3$. Bis(trimethylsilyl)acetylene (211 mg, 1.24 mmol) was added to a suspension of complex **1** (300 mg, 0.21 mmol) in dichloromethane (15 cm^3) and the mixture stirred at room temperature for 24 h. The resulting suspension was evaporated to dryness, the residue was extracted with *n*-hexane (4 × 15 cm^3), and the combined extracts were concentrated and chromatographed over silica gel with a diethyl ether/*n*-hexane (1:1) mixture. A pale yellow band was collected (R_f ∼0.6), from which $Me_3SiC{\equiv}C\{C_6H(CHO)$-6-$(OMe)_3$-2,3,4$\}$ (**5**) was obtained as a pale yellow oil by evaporation. Yield: 55 mg, 45%. Colorless crystals were obtained by recrystallization from *n*-hexane. Mp: 85−86 °C. IR: ν(C═O) 1690, ν(C≡C) 2120 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 10.43 (s, CHO, 1H), 7.24 (s, C_6H, 1H), 3.98 (s, MeO, 3H), 3.96 (s, MeO, 3H), 3.92 (s, MeO, 3H), 0.29 ($SiMe_3$, 9H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, ppm): 190.77 (C═O), 166.1, 164.1, 147.6, 132.3, 116.7, 105.5, 105.0 (aryl H), 61.3 (MeO), 61.2 (MeO), 56.2 (MeO), −0.34 ($SiMe_3$). Mass spectrum: *m*/*z* (% abundance) 219 (M$^+$ − $SiMe_3$, 100), 218 (22), 217 (28), 216 (24), 204 (13). Anal. Calcd for $C_{15}H_{20}O_4Si$: C, 61.62; H, 6.89. Found: C, 61.59; H, 6.99.

Reaction of $[Pd(R^1)Cl(bpy)]$ (bpy = 2,2′-Bipyridine) (6) with PhC≡CPh. Complex **6** (182 mg, 0.37 mmol), PhC≡CPh (263 mg, 1.48 mmol), and $AgClO_4$ (77 mg, 0.37 mmol) were mixed in dichloromethane (10 cm^3) and stirred for 30 min. The mixture was then filtered, giving a solid containing AgCl and **8a**. The filtrate was evaporated and the residue extracted with Et_2O. The combined extracts were filtered over anhydrous $MgSO_4$, giving a solution which, after concentration and

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addition of *n*-hexane, gave 4,5,6-trimethoxy-2,3-diphenyl-1*H*-indenol (**3**). Yield: 101 mg, 73%. Mp: 156−157 °C. IR: ν(OH) 3497 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 7.35 (m, Ph, 5H), 7.18 (m, Ph, 5H), 7.10 (s, H7, 1H), 5.58 (d, $^3J_{HH}$ = 8.4, C*H*OH, 1H), 3.94 (s, MeO, 3H), 3.84 (s, MeO, 3H), 3.28 (s, MeO, 3H), 1.85 (d, $^3J_{HH}$ = 8.4, OH, 1H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, ppm): 153.1, 148.8, 143.4, 142.3, 140.7, 139.3, 136.5, 134.2, 129.3, 129.1, 126.7, 126.2, 128.0, 127.3, 126.9, 104.6 (C7), 77.3 (CHOH), 61.2 (MeO), 61.0 (MeO), 56.4 (MeO). Mass spectrum: *m*/*z* (% abundance) 374 (M^+, 100), 359 (31), 215 (32), 113 (39). Anal. Calcd for $C_{24}H_{22}O_4$: C, 76.99; H, 5.92. Found: C, 76.58; H, 5.87.

Reactions of [Pd(R^1)(MeCN)(bpy)]ClO$_4$ (7). With PhC≡CPh. Complex **7** (73 mg, 0.12 mmol) and PhC≡CPh (43 mg, 0.24 mmol) were mixed in dichloromethane (8 cm^3) and stirred for 15 min. The mixture was then filtered, giving solid [Pd(μ-OH)(bpy)]$_2$(ClO$_4$)$_2$ **(8a)**[17,24] (36 mg, 79%). The filtrate was evaporated and the residue extracted with Et_2O. The combined extracts were filtered over anhydrous $MgSO_4$ and concentrated. Addition of *n*-hexane gave indenol **3**. Yield: 30 mg, 67%.

With PhC≡CPh under Anhydrous Conditions. Complex **7** (77 mg, 0.13 mmol), PhC≡CPh (46 mg, 0.26 mmol), and freshly distilled acetonitrile (over P_2O_5, under nitrogen, 8 cm^3) were mixed under nitrogen in a Carius tube. The tube was sealed and heated at 80 °C for 48 h. After it was cooled, the resulting mixture was filtered over $MgSO_4$, the solution evaporated to dryness, and the residue worked up as described above for the synthesis of **2**. Yield: 30 mg of compound **2**, 64%.

Reactions of [Pd(R^2)(MeCN)(bpy)]ClO$_4$ (9). With PhC≡CPh. Complex **9** (40 mg, 0.07 mmol) and PhC≡CPh (24 mg, 0.13 mmol) were mixed in dichloromethane (5 cm^3) and stirred for 8 h. The resulting suspension was then filtered, giving solid **8a** (52 mg, 98%) and a solution which was subsequently evaporated to dryness. The residue was extracted with hot *n*-hexane. Cooling the resulting solution to room temperature causes the crystallization of the indenol 5,6,7-trimethoxy-2,3-diphenyl-1*H*-indenol (**10**). Yield: 24 mg, 96%. Mp: 140−141 °C. IR: ν(OH) 3491 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 7.42−7.17 (m, 2Ph, 10H), 6.46 (s, H4, 1H), 5.85 (d, $^3J_{HH}$ = 5.6, C*H*OH, 1H), 4.14 (s, MeO, 3H), 3.89 (s, MeO, 3H), 3.79 (s, MeO, 3H), 2.28 (d, $^3J_{HH}$ = 5.6, OH, 1H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, ppm): 154.9, 150.4, 143.7, 140.9, 140.3, 139.3, 134.8, 129.3, 129.1, 128.9, 128.2, 128.0, 127.9, 127.3, 126.9, 100.8 (C7), 75.7 (CHOH), 61.2 (MeO), 60.7 (MeO), 56.4 (MeO). Mass spectrum: *m*/*z* (% abundance) 374 (M^+, 100), 343 (26), 113 (22), 105 (48). Anal. Calcd for $C_{24}H_{22}O_4$: C, 76.99; H, 5.92. Found: C, 76.82; H, 6.00.

With PhC≡CPh under Anhydrous Conditions. Complex **9** (122 mg, 0.20 mmol) and PhC≡CPh (72 mg, 0.40 mmol) were mixed under nitrogen in freshly distilled acetonitrile (over P_2O_5, under nitrogen, 8 cm^3) in a Carius tube and heated at 80 °C for 48 h. The resulting mixture was filtered over $MgSO_4$, the filtrate evaporated to dryness, and the residue extracted with Et_2O. The resulting solution contained the products **10**, **11**, and R^{2}H (molar ratio approximately 3:1:1). It was evaporated almost to dryness and *n*-hexane added, precipitating red 5,6,7-trimethoxy-2,3-diphenylindenone (**11**). Yield: 28 mg, 38%. A crystalline sample was obtained from Et_2O. Mp: 150−151 °C. IR: ν(C=O) 1691 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 7.35 (m, Ph, 5H), 7.22 (m, Ph, 5H), 6.46 (s, H4, 1H), 4.17 (s, MeO, 3H), 3.85 (s, MeO, 3H), 3.84 (s, MeO, 3H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, ppm): 192.9 (C=O), 157.4, 153.0, 152.4, 142.9, 141.8, 133.0, 132.7, 130.8, 130.0, 129.1, 129.0, 128.8, 128.6, 127.9, 127.6, 103.0 (C4), 62.3 (MeO), 61.4 (MeO), 56.5 (MeO). Mass spectrum: *m*/*z* (% abundance) 372 (M^+, 38), 215 (47), 183 (78), 159 (73), 157 (83), 156 (47), 149 (76), 119 (44), 113 (41), 105 (44), 104 (41), 103 (54). Anal. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.53; H, 5.40.

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Reaction of [Pd(η^2-R^2)(μ-Cl)]$_2$ (12) with PhC≡CPh. PhC≡CPh (148 mg, 0.83 mmol) was added to a solution of complex **12** (112 mg, 0.17 mmol) in dichloromethane (10 cm^3). The mixture was stirred for 113 h at room temperature, filtered through Celite, and evaporated to dryness. A ^{1}H NMR spectrum of the resulting residue showed an indenol **10**/indenone **11** molar ratio of *ca.* 1:1. In the mixture, PhC≡CPh and small amounts of Ph_6C_6 and R^{2}H were also detected. When the reaction was carried out under the same conditions but using equimolar amounts of **12** and PhC≡CPh, the resulting indenol/indenone ratio was not affected.

General Procedure for the Preparation of 1-Methylindenols from [Pd(η^2-R^3)(bpy)](CF$_3$SO$_3$) (13) and Alkynes. PhC≡CPh. To a suspension of complex **13** (150 mg, 0.24 mmol) in dichloromethane was added PhC≡CPh (53 mg, 0.30 mmol), and the mixture was stirred at room temperature for 3 h. [Pd(μ-OH)(bpy)]$_2$(CF_3SO_3)$_2$ (**8b**; 90 mg, 87%) was isolated by filtration as a beige solid. The filtrate was evaporated to *ca.* 2 cm^3 and Et_2O added to precipitate white 4,5,6-trimethoxy-1-methyl-2,3-diphenyl-1*H*-indenol (**14**; 29 mg). Further **14** (35 mg) was obtained by evaporation of the ether solution and addition of *n*-hexane. Total yield: 69%. Mp: 169−171 °C. IR: ν(OH) 3462 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 7.37−7.16 (m, Ph, 10H), 6.96 (s, H7, 1H), 3.94 (s, MeO, 3H), 3.84 (s, MeO, 3H), 3.29 (s, MeO, 3H), 2.05 (s, OH, 1H), 1.55 (s, Me1, 3H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, ppm): 154.1, 148.8, 145.9, 145.9, 143.0, 138.3, 136.2, 134.8, 129.6, 129.5, 127.8, 127.5, 127.0, 126.9, 126.7, 102.6 (C7), 83.2 (C1), 61.04 (MeO), 61.00 (MeO), 56.4 (MeO), 24.6 (Me1). Mass spectrum: *m*/*z* (% abundance) 388 (M^+, 97), 373 (34), 266 (15), 216 (31), 215 (100), 213 (30), 202 (17), 172 (25), 164 (18), 155 (40), 77 (17). Anal. Calcd for $C_{25}H_{24}O_4$: C, 77.30; H, 6.23. Found: C, 77.08; H, 6.30.

[Pd(μ-OH)(bpy)]$_2$(CF$_3$SO$_3$)$_2$ (8b). IR: ν(OH) 3485, 3339 cm^{-1}. Anal. Calcd for $C_{22}H_{18}N_4O_8F_6S_2Pd_2$: C, 30.82; H, 2.12; N, 6.54; S, 7.48. Found: C, 31.12; H, 2.06; N, 6.48; S, 7.39. The IR spectrum of this compound is identical with that of [Pd(μ-OH)(bpy)]$_2$(CF_3SO_3)$_2$ prepared by following a published procedure.[24]

ToC≡CTo (To = *p*-Tolyl). 4,5,6-Trimethoxy-1-methyl-2,3-bis(4-tolyl)-1*H*-indenol (**15**) was prepared similarly from **13** (287 mg, 0.46 mmol) and bis(*p*-tolyl)acetylene (100 mg, 0,48 mmol). Reaction time: 1.5 h. The dichloromethane solution was evaporated to dryness, the residue redissolved in Et_2O, and the resulting solution filtered through Celite and concentrated. *n*-Pentane was then added, precipitating **15** as a white solid. Yield: 167 mg, 87%. Mp: 189−191 °C. IR: ν(OH) 3456 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 7.25 (d, *p*-To, 2H, $^3J_{HH}$ = 8 Hz), 7.19 (d, *p*-To, 2H, $^3J_{HH}$ = 8 Hz), 7.07 (d, *p*-To, 2H, $^3J_{HH}$ = 8 Hz), 6.99 (d, *p*-To, 2H, $^3J_{HH}$ = 8 Hz), 6.94 (s, H7, 1H), 3.92 (s, MeO, 3H), 3.83 (s, MeO, 3H), 3.31 (s, MeO, 3H), 2.33 (s, MeC_6H_4, 3H), 2.27 (s, MeC_6H_4, 3H), 2.05 (s, OH, 1H), 1.53 (s, Me1, 3H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, ppm): 152.9, 148.8, 146.1, 145.6, 143.0, 137.8, 136.5, 136.5, 133.4, 132.0, 129.5, 129.4, 128.6, 128.3, 127.0, 102.6 (C7), 83.1 (C1), 61.2 (MeO), 61.1 (MeO), 56.4 (MeO), 24.7 (Me), 21.4 (Me), 21.3 (Me). Mass spectrum: *m*/*z* (% abundance) 416 (M^+, 60), 401 (25), 324 (19), 309 (30), 178 (21), 162 (36), 148 (20), 126 (24), 119 (36), 115 (20), 113 (25), 105 (29), 92 (100), 91 (95), 65 (36). Anal. Calcd for $C_{27}H_{28}O_4$: C, 77.86; H, 6.78. Found: C, 77.52; H, 7.06.

MeO$_2$C≡CO$_2$Me. 4,5,6-Trimethoxy-2,3-bis(methoxycarbonyl)-1-methyl-1*H*-indenol (**16**) was similarly prepared from **13** (200 mg, 0.32 mmol) and the alkyne (46 mg, 0.32 mmol). Reaction time: 3.25 h. The dichloromethane solution was evaporated to dryness, the residue redissolved in Et_2O, and the resulting solution filtered through Celite and concentrated. The white product was crystallized by addition of *n*-hexane and cooling. Yield: 80 mg, 71%. Mp: 107−109 °C. IR: ν(OH) 3497 cm^{-1}, ν(C=O) 1739, 1707 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 6.89 (s, H7, 1H), 3.96 (s, MeO, 3H), 3.94 (s, MeO, 3H), 3.90 (s, MeO, 3H), 3.84 (s, 2MeO, 6H), 3.13 (s, OH, 1H), 1.70 (s, Me1, 3H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, ppm):

166.4, 163.3, 156.5, 148.9, 146.5, 142.3, 142.0, 134.0, 122.1, 102.6 (C7), 81.7 (C1), 61.4 (MeO), 60.8 (MeO), 56.4 (MeO), 52.3 (MeO), 51.8 (MeO), 25.5 (Me1). Mass spectrum: *m*/*z* (% abundance) 352 (M^+, 2), 320 (2), 117 (13), 116 (12), 115 (13), 102 (10), 101 (11), 91 (12), 90 (11), 89 (14), 77 (21), 59 (100). Anal. Calcd for $C_{17}H_{20}O_8$: C, 57.95; H, 5.72. Found: C, 57.69; H, 5.76.

MeC≡CMe. 4,5,6-Trimethoxy-1,2,3-trimethyl-1*H*-indenol (**17**) was similarly prepared from **13** (286 mg, 0.46 mmol) and 2-butyne (0.04 cm^3, 0.51 mmol). Reaction time: 1.25 h. The dichloromethane solution was evaporated to dryness, the residue redissolved in Et_2O, and the resulting solution filtered through Celite and chromatographed over silica gel using a Et_2O/*n*-hexane (1:1) solution; the major colorless band was collected. The solution obtained was dried over anhydrous $MgSO_4$ and evaporated. The residue was recrystallized from *n*-hexane, giving **17** as a white solid. The mother liquor was concentrated and recrystallized, giving a second fraction of **17**. Yield: 81 mg, 67%. Mp: 47−49 °C. IR: ν(OH): 3490 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 6.84 (s, H7, 1H), 3.88 (s, MeO, 3H), 3.87 (s, MeO, 3H), 3.86 (s, MeO, 3H), 2.10 (q, Me3, $^5J_{HH}$ = 1.2 Hz, 3H), 1.82 (q, Me2, 3H), 1.41 (s, Me1, 3H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, ppm): 151.9, 147.7, 145.7, 142.6, 141.6, 130.5, 128.1, 102.7 (C7), 82.0 (C1), 61.6 (MeO), 60.9 (MeO), 56.5 (MeO), 23.4 (Me1), 12.5 (Me), 8.7 (Me). Mass spectrum: *m*/*z* (% abundance) 264 (M^+, 58), 249 (100), 231 (57), 219 (46), 191 (48), 173 (59), 115 (56), 91 (31). Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 67.99; H, 7.67.

^{1}H NOEDIFF (300 MHz, $CDCl_3$): irradiation at 6.84 ppm (H7) induced an enhancement at 3.88 ppm (singlet, 3%, MeO6); irradiation at 1.41 ppm (Me1) induced enhancements at 6.84 ppm (16%, H7) and 1.82 ppm (3%, Me2).

EtC≡CEt. 2,3-Diethyl-4,5,6-trimethoxy-1-methyl-1*H*-indenol (**18**) was similarly prepared from **13** (303 mg, 0.49 mmol) and 3-hexyne (42 mg, 0.51 mmol). Reaction time: 2 h. The dichloromethane solution was chromatographed (silica gel, Et_2O/hexane 1:1). The bulk colorless band was collected. The solution obtained was dried over anhydrous $MgSO_4$ and evaporated *in vacuo* to get a colorless oil. Yield: 131 mg, 91%. IR: ν(OH) 3354 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 6.82 (s, H7, 1H), 3.92, 3.88, 3.86 (3s, 3MeO, 9H), 2.51 (q, CH_2, $^3J_{HH}$ = 7.8 Hz, 2H), 2.43−2.21 (m ABX_3, CH_2, $^3J_{AX}$ = 7.8 Hz, $^2J_{AB}$ = 13.8 Hz, $\delta_A - \delta_B$ = 0.13 ppm, 2H), 1.64 (s, OH, 1H), 1.47 (s, Me1, 3H), 1.16 (t, CH_2CH_3, $^3J_{HH}$ = 7.8 Hz, 3H), 1.15 (t, CH_2-CH_3, $^3J_{HH}$ = 7.8 Hz, 3H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, ppm): 151.9, 147.4, 146.6, 146.0, 142.2, 137.6, 126.7 (quaternary carbons), 102.3 (C7), 82.5 (C1), 61.2, 60.7, 56.3 (3MeO), 23.9 (Me1), 20.0, 17.3 ($2CH_2$), 15.0, 14.2 ($2CH_2Me$). Mass spectrum: *m*/*z* (% abundance) 292 (M^+, 61), 277 (30), 264 (16), 263 (100), 248 (31), 233 (28), 232 (30), 128 (16), 115 (29), 91 (19), 77 (18). Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 69.55; H, 8.60.

PhC≡CCO$_2$Et. 2-(Ethoxycarbonyl)-4,5,6-trimethoxy-1-methyl-3-phenyl-1*H*-indenol (**19a**) and 3-(ethoxycarbonyl)-4,5,6-trimethoxy-1-methyl-2-phenyl-1*H*-indenol (**19b**) were similarly prepared from **13** (300 mg, 0.48 mmol) and ethyl phenylpropiolate (83 μL, 0.50 mmol). Reaction time: 2 h. The dichloromethane solution was evaporated, and Et_2O (30 cm^3) was added. An insoluble brown solid was isolated by filtration and washed with Et_2O. The ether solution was found to be a 1:1.3 mixture of **19a** and **19b**. It was chromatographed over silica gel using acetone/hexane (1:3), and two bands (R_f 0.33 and 0.25) were collected. The separation was visualized using 265 nm UV light, as both indenols are colorless (under UV irradiation; the first band is blue and the second yellow). The two bands contained 4.8:1 (first band) and 1:8.2 (second band) mixtures of **19a** and **19b**, respectively. Further chromatography (under the same conditions) gave two solutions which were dried with anhydrous $MgSO_4$ and evaporated to dryness, yielding pure indenols as colorless oils. In some preparations, **19b** appeared as a light pink oil due to the presence of an impurity in a spectroscopically undetectable amount. Crystalline samples can be obtained from *n*-hexane.

19a: yield (of the crude product) 47 mg, 25%. Mp: 85−87 °C. IR: ν(OH) 3516 cm^{-1}, ν(C=O) 1698, 1670 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): 7.40−7.32 (m, Ph, 5H), 6.96 (s, H7, 1H), 4.13−3.93 (m ABX_3, $J_{AX} = J_{BX}$ = 7.2 Hz, J_{AB} = 10.8 Hz, $\delta_A - \delta_B$ = 0.077 ppm, CH_2, 1H), 3.95 (s, MeO6, 3H), 3.82 (s, OH, 1H), 3.79 (s, MeO5, 3H), 3.31 (s, MeO4, 3H), 1.74 (s, Me1, 3H), 0.93 (t, part X of ABX_3, *Me*CH_2, 3H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, ppm): 165.2 (C=O), 155.8, 152.1, 150.8, 146.8, 143.0, 137.0, 134.8, 128.0, 127.8, 127.5, 127.2, 102.4 (C7), 81.6 (C1), 61.1, 61.0, 60.1, 56.4 (3 MeO and CH_2O), 26.3 (Me1), 13.6 ($MeCH_2$). Mass spectrum: *m*/*z* (% abundance) 384 (M^+, 88), 324 (24), 323 (100), 311 (38), 310 (88), 165 (37), 161 (21), 154 (24), 153 (40), 152 (38), 139 (44), 138 (27), 129 (27), 126 (35), 115 (24), 91 (23), 77 (25). Anal. Calcd for $C_{22}H_{24}O_6$: C, 68.74; H, 6.29. Found: C, 68.95; H, 6.28.

^{1}H NOEDIFF (300 MHz, $CDCl_3$): irradiation at 6.96 ppm (H7) induced enhancements at 3.95 ppm (5%, MeO6) and at 1.74 ppm (1%, Me1); irradiation at 3.31 ppm (MeO4) induced an enhancement at 7.37−7.31 (multiplet, 3%, Ph); irradiation at 1.74 ppm (Me1) induced a 17% enhancement at 6.96 ppm (singlet, H7).

19b: yield (of the crude product) 63 mg, 34%. Mp: 87−89 °C. IR: ν(OH) 3472 cm^{-1}, ν(C=O) 1716 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.71−7.67, 7.39−7.32 (2m, Ph, 5H), 6.87 (s, H7, 1H), 4.37−4.24 (m ABX_3, $^2J_{AB}$ = 10.8 Hz, $^3J_{BX} = {}^3J_{AX}$ = 7.2 Hz, $\delta_A - \delta_B$ = 0.062 ppm, CH_2, 2H), 3.91 (s, MeO, 3H), 3.89 (s, MeO, 3H), 3.86 (s, MeO, 3H), 2.13 (s, OH, 1H), 1.51 (s, Me1, 3H), 1.27 (t, $MeCH_2$, 3H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, ppm): 167.7 (C=O), 153.8, 147.3, 146.6, 144.9, 142.6, 133.4, 129.6, 128.2, 128.2, 127.9, 124.1, 102.7 (C7), 83.8 (C1), 61.2, 61.2, 60.8, 56.4 (3 MeO and CH_2O), 24.1 (Me1), 13.9 ($MeCH_2$). Mass spectrum: *m*/*z* (% abundance) 384 (M^+, 100), 339 (27), 338 (96), 323 (54), 311 (53), 310 (57), 165 (42), 153 (33), 152 (37), 139 (79), 115 (35), 105 (48), 78 (38), 77 (40). Anal. Calcd for $C_{22}H_{24}O_4$: C, 68.74; H, 6.29. Found: C, 68.93; H, 6.34.

^{1}H NOEDIFF (300 MHz, $CDCl_3$): irradiation at 6.87 ppm (H7) induced enhancements at 3.90 ppm (6%, MeO6) and at 1.51 ppm (2%, Me1); irradiation at 1.51 ppm induced enhancements at 7.71−7.67 ppm (multiplet, 11%, Ph) and at 6.86 ppm (20%, H7).

^{t}BuC≡CMe. 2-*tert*-Butyl-4,5,6-trimethoxy-1,3-dimethyl-1*H*-inden-1-ol (**20a**) and 3-*tert*-butyl-4,5,6-trimethoxy-1,2-dimethyl-1*H*-inden-1-ol (**20b**) were similarly prepared from **13** (384 mg, 0.62 mmol) and 4,4-dimethyl-2-pentyne (86 mg, 0.90 mmol). Reaction time: 25 h. The dichloromethane solution was chromatographed (silica gel, Et_2O/hexane 2:3). The colorless bulk band was collected. The resulting solution was dried over anhydrous $MgSO_4$ and evaporated to give a colorless oil which contained (by ^{1}H NMR spectroscopy) a 1:1 mixture of **20a** and **20b**. Attempts to separate this mixture were unsuccessful. Yield: 160 mg, 84%. IR: ν(OH) 3304 (br) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 6.83 (s, H7 of **20b**, 1H), 6.73 (s, H7 of **20a**, 1H), 3.95 (s, MeO4 of **20b**, 3H), 3.89 (s, MeO6 of **20b**, 3H), 3.87 (2s, MeO4 and 6 of **20a**, 6H), 3.84, 3.82 (2s, MeO5 of **20a** and **20b**, 6H), 2.32 (s, Me3 of **20a**, 3H), 2.05 (s, Me2 of **20b**, 3H), 1.66 (s, OH, 1H), 1.63 (s, Me1 of **20a**, 3H), 1.49 (s, OH, 1H), 1.40 (2s, 2 ^{t}Bu, 18H), 1.36 (s, Me1 of **20b**, 3H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, ppm): 152.1, 151.9, 151.1, 148.0, 147.6, 146.9, 146.5, 142.53, 142.45, 142.41, 139.3, 132.7, 127.3, 126.6 (quaternary carbons), 101.6, 101.5 (2 C7), 84.6, 84.2 (2 C1), 61.4, 60.9, 60.4, 60.2, 56.4, 56.2 (6MeO), 34.9, 34.1 (2 quaternary carbons of ^{t}Bu groups), 31.1 (6Me of ^{t}Bu), 26.2, 24.3 (2 Me1), 15.5, 12.0 (Me2 of **20b** and Me3 of **20a**). Mass spectrum: *m*/*z* (% abundance) 306 (M^+, 19), 250 (25), 249 ($M^+ - {}^t$Bu, 98), 235 (24), 234 (51), 219 (26), 145 (25), 131 (27), 129 (49), 128 (52), 117 (27), 115 (66), 103 (26), 91 (52), 77 (48), 65 (27), 59 (100), 57 (67), 55 (40), 53 (32), 51 (27). Anal. Calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found: C, 70.62; H, 8.62.

^{1}H NOEDIFF (300 MHz, $CDCl_3$): irradiation at 6.83 ppm (H7 of **20b**) induced an enhancement at 3.89 ppm (6%, MeO6 of **20b**); irradiation at 6.73 ppm (H7 of **20a**) induced enhancements at 3.87 ppm (5%, MeO4 and 6 of **20a**) and 1.63 ppm

(2%, Me1 of **20a**); irradiation at 2.32 ppm (Me3 of **20a**) induced enhancements at 3.87 ppm (8%, MeO4 and 6 of **20a**) and 1.40 ppm (<1%, ^{t}Bu of both isomers); irradiation at 2.05 ppm (Me2 of **20b**) induced enhancements at 1.40 ppm (<1%, ^{t}Bu) and 1.36 ppm (1%, Me1 of **20b**); irradiation at 1.63 ppm induced an enhancement at 6.73 ppm (23%, H7 of **20a**); irradiation at 1.40 ppm induced enhancements at 3.95 ppm (41%, MeO4 of **20b**), 2.32 ppm (19%, Me3 of **20a**), 2.05 ppm (21%, Me2 of **20b**), 6.83 (26%), and 6.73 ppm (17%), the latter probably being produced by partial saturation of the signals at 1.63 (Me1 of **20a**) and 1.36 ppm (Me1 of **20b**), respectively.

PhC≡CC$_6$H$_4$NO$_2$-4. 4,5,6-Trimethoxy-1-methyl-3-(4-nitrophenyl)-2-phenyl-1*H*-indenol (**21a**) and 4,5,6-trimethoxy-1-methyl-2-(4-nitrophenyl)-3-phenyl-1*H*-indenol (**21b**) were similarly obtained from **13** (120 mg, 0.19 mmol) and (4-nitrophenyl)phenylacetylene (47 mg, 0.21 mmol). Reaction time: 3 h. The dichloromethane solution was evaporated to dryness, the residue redissolved in Et_2O, and the solution filtered through Celite and evaporated. The resulting mixture was found to be composed of **21a**, **21b**, and the starting alkyne in a 1:2:0.1 ratio (by ^{1}H NMR spectroscopy). Recrystallization from dichloromethane/pentane solution gave a yellow solid which was a mixture of both isomers. Attempts to separate this mixture were unsuccessful**.** Yield: 69 mg, 84%. IR: ν(OH) 3502 cm^{-1}, ν(NO$_2$) 1508, 1338 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 8.13 (d, H ortho to NO$_2$ of **21a**, $^3J_{HH}$ = 9.0 Hz, 2H), 8.01 (d, H *ortho* to NO$_2$ of **21b**, $^3J_{HH}$ = 9.3 Hz, 2H), 7.57 (d, H *meta* to NO$_2$ of **21b**, 2H), 7.47 (d, H *meta* to NO$_2$ of **21a**, 2H), 7.32−7.20 (m, Ph of **21a** and **21b**, 10H), 6.974 (s, H7 of **21a**, 1H), 6.967 (s, H7 of **21b**, 1H), 3.953 (s, MeO of **21b**, 3H), 3.947 (s, MeO of **21a**, 3H), 3.85 (s, MeO of **21a**, 3H), 3.84 (s, MeO of **21b**, 3H), 3.36 (s, MeO of **21a**, 3H), 3.32 (s, MeO of **21b**, 3H), 2.19 (s, OH of **21b**, 1H), 2.11 (s, OH of **21a**, 1H), 1.55 (2s, Me1 of **21a** and **21b**, 6H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, ppm): 154.0, 153.6, 149.4, 148.5, 148.3, 146.8, 146.3, 146.2, 145.6, 143.6, 143.2, 143.0, 142.9, 142.1, 141.7, 136.2, 135.6, 134.0 (quaternary carbons), 130.8, 129.9, 129.5, 129.3, 128.3, 128.1, 127.8, 127.7 (CH Ar), 126.1, 125.5 (quaternary carbons), 123.1, 122.8 (CH Ar), 102.8, 102.5 (2C7), 83.4, 83.3 (2C1), 61.11, 61.07 (br), 61.0, 56.51, 56.50 (6MeO), 24.7, 24.5 (2Me1). Mass spectrum: *m*/*z* (% abundance) 433 (M$^+$, 100), 418 (55), 239 (30), 226 (31), 216 (30), 215 (87), 214 (39), 213 (78), 202 (33), 189 (34), 178 (31), 155 (30), 126 (34), 120 (62), 113 (47), 106 (36). Anal. Calcd for $C_{25}H_{23}NO_6$: C, 69.27; H, 5.35; N, 3.23. Found: C, 69.02; H, 5.42; N, 3.44.

^{1}H NOEDIFF (300 MHz, $CDCl_3$): irradiation at 1.55 ppm (Me1 of both isomers) induced enhancements at 7.57 ppm (doublet, 8%, H3 of the C$_6$H$_4$NO$_2$ of **21b**), at 7.30−7.24 (multiplet, 2%, Ph of **21a**), and at 6.97 (singlet, 13%, H7 of **21a** and **21b**); irradiation at 2.19 ppm (OH of **21b**) produces saturation of both OH signals by proton exchange, which induced enhancements at 8.01 ppm (doublet, −1%, H2 of the C$_6$H$_4$NO$_2$ of **21b**), at 7.57 ppm (doublet, 6%, H3 of the C$_6$H$_4$-NO$_2$ of **21b**), at 7.30−7.24 (multiplet, 2%, Ph of **21a**), and at 6.97 ppm (singlet, 6%, H7 of **21a** and **21b**).

PhC≡CC$_6$H$_4$OMe-4. 4,5,6-Trimethoxy-3-(4-methoxyphenyl)-1-methyl-2-phenyl-1*H*-indenol (**22a**) and 4,5,6-trimethoxy-2-(4-Methoxyphenyl)-1-methyl-3-phenyl-1*H*-indenol (**22b**) were similarly obtained from **13** (194 mg, 0.31 mmol) and (4-methoxyphenyl)phenylacetylene (71 mg, 0.34 mmol). Reaction time: 2 h. The dichloromethane solution was evaporated, the residue redissolved in Et_2O, and the solution filtered through Celite and evaporated to dryness. The resulting mixture was found to be composed of **22a**, **22b**, and the starting alkyne in a 2:1:0.4 ratio (by ^{1}H NMR spectroscopy). It was chromatographed over silica gel using a Et_2O/hexane (1:1) solution. The bulk colorless band was taken. The solution obtained was dried over anhydrous $MgSO_4$ and evaporated, giving a colorless oil which was a mixture of both regioisomers. Attempts to separate this mixture were unsuccessful. Yield: 124 mg, 96%. IR: ν(OH) 3372 (br) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.36−7.18 (m, Ph of **22a** and **22b** + H3 of **22a** and **22b** C$_6$H$_4$-OMe group, 14H), 6.96 (2s, H7 of **22a** and **22b**, 2H), 6.80 (d, H2 of **22a** C$_6$H$_4$OMe group, $^3J_{HH}$ = 9.0 Hz, 2H), 6.72 (d, H2 of **22b** C$_6$H$_4$OMe group, $^3J_{HH}$ = 9.3 Hz, 2H), 3.94 (2s, 2MeO6, 6H), 3.85 (s, MeO of **22a**, 3H), 3.84 (s, MeO of **22b**, 3H), 3.80 (s, MeOC$_6$H$_4$ of **22a**, 3H), 3.75 (s, MeOC$_6$H$_4$ of **22b**, 3H), 3.33 (s, MeO of **22a**, 3H), 3.29 (s, MeO of **22b**, 3H), 2.00 (s br, 2OH, 2H), 1.55 (s, Me1 of **22b**, 3H), 1.54 (s, Me1 of **22a**, 3H). ^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): 158.5, 158.4, 153.0, 152.9, 148.8, 148.6, 146.1, 146.0, 145.5, 145.3, 142.9, 137.9, 137.1, 136.6, 135.1 (quaternary carbons), 130.9, 130.6, 129.6, 129.5 (CH Ar), 128.6 (quaternary carbons), 127.8, 127.6 (CH Ar), 127.2 (quaternary carbon), 126.9, 126.83 (CH Ar), 126.76 (quaternary carbon), 113.3, 112.9 (CH Ar), 102.6 (2 C7), 83.2, 83.0 (2 C1), 61.2, 61.1 (br), 56.4 (br) (MeO4−6 of **22a** and **22b**), 55.10, 55.06 (MeOC$_6$H$_4$ of **22a** and **22b**), 24.8, 24.6 (2 Me1). Mass spectrum: *m*/*z* (% abundance) 418 (M$^+$, 100), 403 (29), 310 (43), 295 (35), 202 (17), 170 (31), 156 (17), 135 (19), 120 (18), 113 (24), 108 (34), 101 (20), 78 (21), 77 (29). Anal. Calcd for $C_{26}H_{26}O_5$: C, 74.62; H, 6.26. Found: C, 74.37; H, 6.40.

^{1}H NOEDIFF (300 MHz, $CDCl_3$) irradiation at 6.96 ppm (H7 of both isomers) induced enhancements at 3.94 ppm (3%, MeO6 of both isomers) and at 2.00 ppm (4%, OH of both isomers); irradiation at 2.00 ppm (OH of both isomers) induced enhancements at 7.37−7.30 (multiplet, 2%, the Ph multiplet of **22a** overlapped with the doublet assigned to the *meta* protons of the C$_6$H$_4$OMe group of **22b**; the chemical shifts of the *meta* proton doublets of the C$_6$H$_4$OMe groups of **22a** and **22b** were determined by ^{1}H decoupling irradiating the ortho proton doublets) and at 6.96 ppm (4%, H7); irradiation at 1.55 ppm (Me1 of both isomers) induced enhancements at 7.37−7.30 (multiplet, 3%) and at 6.96 ppm (12%, H7). The values of these enhancements are not corrected for partial saturation.

PhC≡CMe. 4,5,6-Trimethoxy-1,3-dimethyl-2-phenyl-1*H*-indenol (**23a**) was similarly prepared from **13** (130 mg, 0.21 mmol) and 1-phenyl-1-propyne (28 mg, 0.24 mmol). Reaction time: 2 h. The dichloromethane solution was evaporated, the residue redissolved in Et_2O, the solution filtered through Celite, and the compound obtained as a white solid by recrystallization from Et_2O/hexane. Yield: 54 mg, 79%. Mp: 188−191 °C. IR: ν(OH) 3274 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.50−7.25 (m, Ph, 5H), 6.87 (s, H7, 1H), 3.93 (s, MeO4, 3H), 3.91 (s, MeO6, 3H), 3.88 (s, MeO5, 3H), 2.19 (s, Me3, 3H), 1.84 (s, OH, 1H), 1.43 (s, Me1, 3H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, ppm): 152.7, 148.6, 145.6, 144.9, 142.6, 135.3, 134.1, 129.3, 128.1, 127.3, 127.1, 102.4 (C7), 82.9 (C1), 61.5 (MeO), 60.8 (MeO), 56.4 (MeO), 24.2 (Me1), 13.8 (Me3). Mass spectrum: *m*/*z* (% abundance) 326 (M$^+$, 100), 311 (72), 266 (55), 233 (32), 219 (31), 208 (49), 207 (37), 205 (72), 178 (39), 146 (40), 105 (70), 91 (52), 90 (44), 81 (42), 77 (34). Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.54; H, 6.82.

^{1}H NOEDIFF (300 MHz, $CDCl_3$): irradiation at 6.87 ppm (H7) induced enhancements at 3.91 ppm (6%, MeO6), at 1.84 ppm (4%, OH), and at 1.43 ppm (2%, Me1); irradiation at 2.19 ppm (Me3) induced enhancements at 7.48−7.45 ppm (multiplet, 5%, Ph) and at 3.93 ppm (8%, MeO4); irradiation of the 1.84 ppm singlet induced enhancements at 7.48−7.45 ppm (multiplet, 2%, Ph) and at 6.87 ppm (4%, H7); irradiation at 1.43 ppm (Me1) induced enhancements at 7.48−7.45 ppm (multiplet, 4%, Ph), at 6.87 ppm (18%, H7), and at 1.84 ppm (10%, OH).

^{t}BuC≡CH. 3-*tert*-Butyl-4,5,6-trimethoxy-1-methyl-1*H*-indenol (**24**) was similarly prepared from **13** (255 mg, 0.41 mmol) and *tert*-butylacetylene (0.06 cm^3, 0.49 mmol). Reaction time: 2 h. The dichloromethane solution was chromatographed over silica gel using a Et_2O/hexane (1:1) solution. The bulk colorless band was collected. The solution obtained was dried with anhydrous $MgSO_4$ and evaporated in *vacuo* to get a colorless oil. Yield: 94 mg, 78%. IR: ν(OH) 3412 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 6.81 (s, H7, 1H), 5.85 (s, H2, 1H), 3.98 (s, MeO4, 3H), 3.89 (s, MeO6, 3H), 3.82 (s, MeO5, 3H), 1.90 (s, OH, 1H), 1.49 (s, Me1, 3H), 1.29 (s, ^{t}Bu, 9H). ^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): 153.1, 152.6, 148.1, 147.8, 142.2, 133.5 (C2), 124.9, 101.9 (C7), 79.4 (C1), 60.5 (MeO), 60.3 (MeO), 56.3 (MeO), 32.9 (quaternary C of ^{t}Bu), 29.4 (3 Me of

^{t}Bu), 24.8 (Me1). Mass spectrum: *m/z* (% abundance) 292 (M^+, 17), 235 (94), 221 (100), 205 (33), 131 (33), 128 (31), 115 (62), 105 (44), 77 (35). Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 69.80; H, 8.43.

^{1}H NOEDIFF (300 MHz, $CDCl_3$): irradiation at 6.81 ppm (H7) induced enhancements at 3.89 ppm (4%, MeO6), 1.90 ppm (5%, OH), and 1.49 ppm (1%, Me1); irradiation at 5.85 ppm (H2) induced enhancements at 1.90 ppm (7%, OH) and 1.29 ppm (1%, ^{t}Bu); irradiation at 1.90 ppm (OH) induced enhancements at 6.81 ppm (7%, H7) and 5.85 ppm (5%, H2); irradiation at 1.49 ppm (Me1) induced enhancements at 6.81 ppm (20%, H7), 5.85 ppm (15%, H2), and 1.90 ppm (11%, OH); irradiation at 1.29 ppm (^{t}Bu) induced enhancements at 5.85 ppm (45%, H2) and 3.98 ppm (10%, MeO4). The sum of the enhancements measured at 5.85 ppm is more than 50%. This can be attributed to the fact that, when the 1.29 ppm signal is irradiated, a small saturation of 1.90 and 1.49 ppm signals is seen in the difference spectrum.

Reactions using [Pd(η^2-R^3)(μ-Cl)]$_2$ (25) and the Chiral Diphosphine (−)-DIOP. With PhC≡CPh. Thallium(I) triflate (55 mg, 0.16 mmol) was added to a suspension of [Pd(η^2-R^3)(μ-Cl)]$_2$ (**25**; 55 mg, 0.08 mmol) in acetonitrile (6 cm^3). The mixture was stirred for 20 min at room temperature and filtered through Celite. (−)-DIOP (78 mg, 0.16 mmol) was added to the resulting yellow solution, and this mixture was stirred for 20 min. The color of the solution changed from bright yellow to pale yellow. The solution was completely evaporated, and a solution of PhC≡CPh (28 mg, 0.16 mmol) in acetone (12 cm^3) was added to the residue. The mixture was stirred at room temperature for 23 h. The resulting orange solution was filtered through Celite and concentrated to *ca.* 2 cm^3 and Et_2O added, precipitating impure [Pd(μ-OH)(DIOP)]$_2$(CF_3SO_3)$_2$ (**8c**; 21 mg, 17%), an orange solid. This was filtered, washed with Et_2O, and dried in air. The orange ether solution was chromatographed over silica gel using a Et_2O/hexane (3:1) solution; a colorless band was collected (R_f aprox. 0.4). The eluate was dried over anhydrous $MgSO_4$ and evaporated *in vacuo* to give **14** as a colorless oil. Yield: 32 mg, 71%.

A sample of **14** was treated with 1 equiv of the chiral NMR shift reagent (+)-[EuL$_3$] (L = 3-((heptafluoropropyl)hydroxymethylene)-(+)-camphorate) in $CDCl_3$. One of the MeO resonances in the ^{1}H NMR spectrum of **14** was seen to exhibit a near base line splitting (0.17 ppm). The ratio of enantiomers determined by integration of these signals was 1:2.

With ToC≡CTo. This procedure was analogous to that followed in the PhC≡CPh reaction, using **25**, thallium(I) triflate, (−)-DIOP, and bis(*p*-tolyl)acetylene. Reaction time: 7 h. The ether solution was chromatographed over silica gel using a Et_2O/hexane (1:1) solution, and a colorless band was collected (R_f ∼0.4). The eluate was dried over anhydrous $MgSO_4$ and evaporated *in vacuo* to give **15** as a pale yellow oil. Yield: 34 mg, 52%.

A sample of **15** was treated with 1.5 equiv of the chiral NMR shift reagent (+)-[EuL$_3$] (L = 3-((heptafluoropropyl)hydroxymethylene)-(+)-camphorate) in $CDCl_3$. One of the MeO resonances in the ^{1}H NMR spectrum of **15** exhibited near base line splitting (0.14 ppm). The enantiomer ratio determined by integration of these signal was 1:2.

With PhC≡CMe. Similarly, thallium(I) triflate (87 mg, 0.25 mmol), **25** (87 mg, 0.125 mmol), (−)-DIOP (124 mg, 0.25 mmol), and 1-phenyl-1-propyne (35 mg, 0.30 mmol) were used. Reaction time: 4 h. The yellow-orange Et_2O solution was chromatographed over silica gel using Et_2O/hexane (1:1) as eluent. A pale yellow band was collected (R_f 0.24); the resulting solution was dried with anhydrous $MgSO_4$ and evaporated *in vacuo*, to give a pale yellow oil. This oil was found to be a 1:10 mixture of 4,5,6-trimethoxy-1,3-dimethyl-2-phenyl-1*H*-indenol (**23a**) and 4,5,6-trimethoxy-1,2-dimethyl-3-phenyl-1*H*-indenol (**23b**). It was not possible to separate this mixture by chromatography. Yield: 56 mg, 69%. IR: ν(OH) 3270 (br) cm^{-1}. ^{1}H NMR (only signals of **23b**; 200 MHz, $CDCl_3$, ppm): 7.44−7.31 (m, Ph, 5H), 6.93 (s, H7, 1H), 3.90 (s, MeO6, 3H), 3.82 (s, MeO5, 3H), 3.28 (s, MeO4, 3H), 1.82 (s, Me2, 3H), 1.78 (s br, OH, 1H), 1.53 (s, Me1, 3H). ^{13}C{^{1}H} NMR only signals of 4,5,6-trimethoxy-1,2-dimethyl-3-phenyl-1*H*-indenol; 75 MHz, $CDCl_3$, ppm): 152.8, 147.8, 145.6, 144.8, 142.9, 136.1, 135.6 (quaternary carbons), 129.3, 127.6 (CH Ph), 127.4 (quaternary carbons), 127.0 (CH Ph), 102.9 (C7), 82.1 (C1), 61.12, 61.09, 56.5 (3MeO), 23.8 (Me1), 9.7 (Me2). Mass spectrum: *m/z* (% abundance) 326 (M^+, 100), 311 (77), 296 (12), 283 (12), 253 (20), 233 (17), 178 (15), 165 (27), 153 (18), 152 (21), 148 (12), 139 (12), 115 (13), 91 (13), 89 (13), 77 (12), 76 (17), 69 (14). Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.57; H, 6.82.

^{1}H NOEDIFF of **23b** (300 MHz, $CDCl_3$): irradiation at 6.93 ppm (H7) induced enhancements at 3.90 ppm (5%, MeO6), at 1.78 ppm (4%, OH), and at 1.53 ppm (1%, Me1); irradiation at 3.28 ppm (MeO4) induced an enhancement at 7.36−7.31 ppm (multiplet, 2%, Ph); irradiation at 1.82 ppm (Me2) induced a 3% enhancement at 7.36−7.31 ppm (multiplet, Ph) and a 4% enhancement at 6.93 ppm, which is probably due to partial saturation of the nearby OH signal (1.77 ppm); irradiation at 1.77 ppm (OH) induced an enhancement at 6.93 ppm (5%, H7); Irradiation at 1.53 ppm induced enhancements at 6.93 ppm (16%, H7) and at 1.82 ppm (3%, Me2).

The mixture of indenols was treated with 0.8 equiv of the chiral NMR shift reagent (+)-[EuL$_3$] (L = 3-((heptafluoropropyl)hydroxymethylene)-(+)-camphorate) in $CDCl_3$. One of the MeO resonances in the ^{1}H NMR spectrum of **23b** exhibited near base line splitting (0.19 ppm). The enantiomer ratio determined by integration of these signals was 1:1.2.

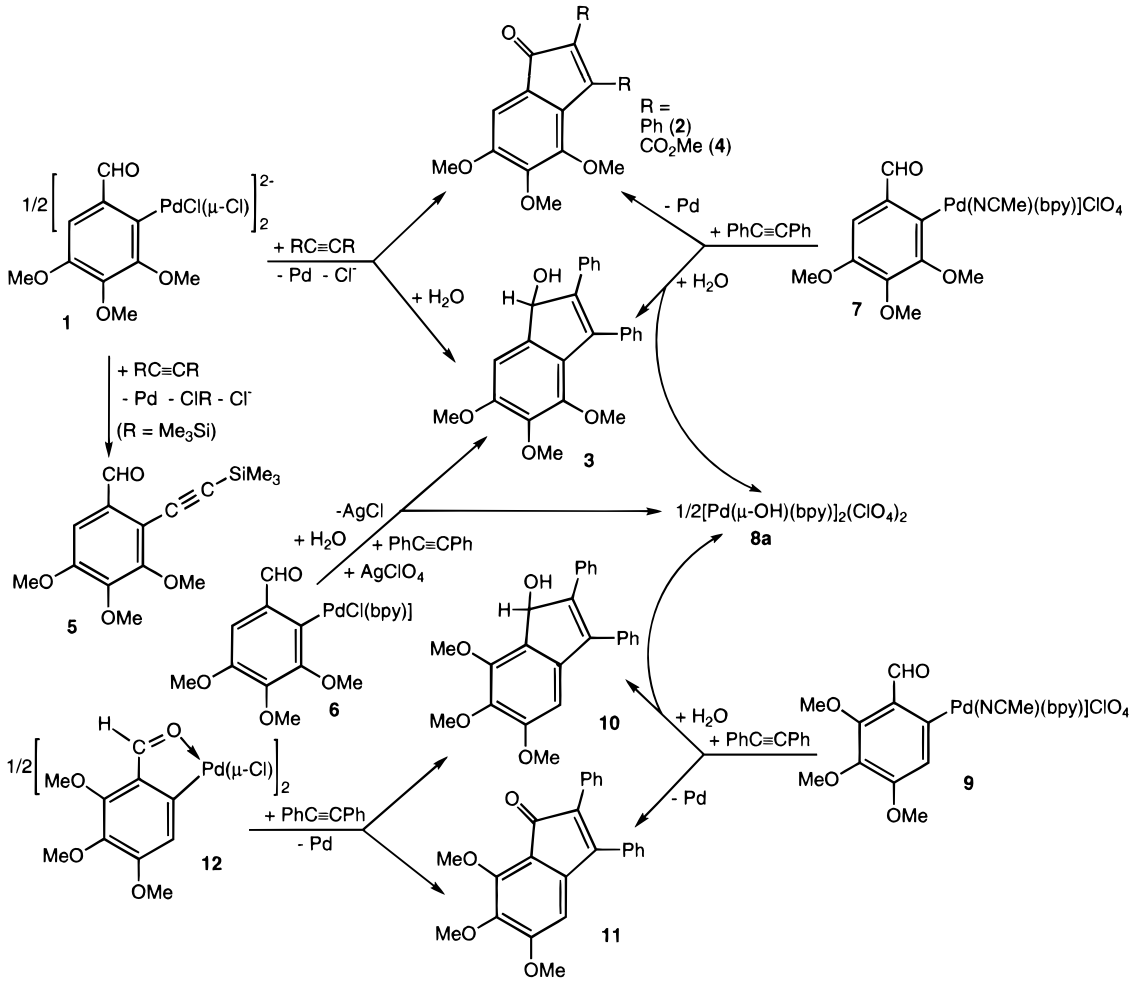
[Pd(μ-OH)(DIOP)]$_2$(CF_3SO_3)$_2$ (8c). IR: ν(OH) 3592 cm^{-1}. Mp: 147 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.66−7.16 (m, Ph, 40H), 3.89 (m, CH, 4H), 2.79−2.60 (m, CH_2, 8H), 1.27 (s, Me, 12H), −2.27 (s, OH, 2H). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, ppm): 20.21 (s). Anal. Calcd for $C_{64}H_{66}O_{12}F_6S_2P_4Pd_2$: C, 49.85; H, 4.31; S, 4.16. Found: C, 49.90; H, 4.42; S, 4.10.

Reaction using [Pd(η^2-R^3)(μ-Cl)]$_2$ (25) and 1,2-Bis(diphenylphosphino)ethane. Complex **25** (52 mg, 0.074 mmol) and thallium(I) triflate (52 mg, 0,15 mmol) were reacted in MeCN (5 cm^3) for 15 min. The resulting suspension was filtered, and 1,2-bis(diphenylphosphino)ethane (59 mg, 0.15 mmol) was added to the filtrate, which was stirred for a further 15 min and then evaporated to dryness. An acetone solution of PhC≡CMe (20 mg, 0.17 mmol) was added to the residue. This mixture was stirred at room temperature for 16.5 h, the resulting suspension filtered through Celite, and the orange solution concentrated to *ca.* 2 cm^3. Diethyl ether was added, and a pale brown solid precipitated. This solid was extracted with diethyl ether (2 × 10 cm^3). The ether solution was chromatographed over silica gel using a Et_2O/hexane (1:1) solution as eluent. A colorless band (R_f ∼0.24) was collected to give a colorless oil, which was found to be a mixture of **23a**, **23b**, and R^{3}H (7:1:1.5, determined by ^{1}H NMR spectroscopy).

Catalytic Syntheses. Synthesis of 3. Hg(R^1)$_2$ (300 mg, 0.51 mmol), PhC≡CPh (545 mg, 3.06 mmol), $CuCl_2$ (137 mg, 1.02 mmol), and (NMe_4)$_2$[$PdCl_6$] (29 mg, 0.05 mmol) were mixed in acetone (15 cm^3) and stirred at room temperature for 96 h. The mixture was filtered, the solution evaporated, and the residue extracted with warm Et_2O. The indenol **3** was crystallized by partial evaporation and addition of *n*-hexane and recrystallized from Et_2O. Yield: 230 mg, 62% (with respect to R^1).

Synthesis of 10-Formyl-6,7-dimethoxy-1,2,3,4-tetraphenylspiro[4.5]-1,3,6,9-decatetraen-8-one (26). Hg(R^1)$_2$ (150 mg, 0.25 mmol), PhC≡CPh (446 mg, 2.5 mmol), $CuCl_2$ (134 mg, 1 mmol), and ($PhCH_2PPh_3$)$_2$[Pd_2Cl_6] (14 mg, 0.01 mmol) were mixed under nitrogen in freshly distilled acetone (over P_2O_5, 10 cm^3). After it was stirred for 28 h at room temperature, the mixture was filtered and the residue extracted with Et_2O (3 × 5 cm^3). The combined extracts were evaporated and the resulting residue extracted with hexane (3 × 5 cm^3). The extracts were chromatographed on a silica gel column. A yellow band was eluted with mixtures of hexane/Et_2O (1:0 to 0:1), the last elution giving a solution which contained the

Scheme 1



impure compound. This solution was chromatographed on an Al_2O_3 column. Elution with mixtures of hexane/dichloromethane (from 1:0 to 1:3) gave a yellow solution from which, after evaporation and drying *in vacuo*, compound **26** was isolated. Yield: 45 mg, 17% (with respect to $Hg(R^1)_2$). Mp: 95−96 °C. IR: ν(C=O) 1698, 1640 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, ppm): 9.48 (s, CHO, 1H), 7.2−7.0, 7.0−6.9 (m, Ph, 20H), 6.84 (s, H9, 1H), 3.99 (s, MeO, 3H), 3.50 (s, MeO, 3H), $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): 190.13 (CHO), 183,81 (C=O), 159.43, 150.38, 143.35, 141.91, 140.70, 134.33, 134.26, 133.78, 129.83, 128,97, 128.26, 127.95, 127.85, 127.54, 68.66 (C spiro), 61.24 (MeO), 60.55 (MeO). Mass spectrum: *m/z* (% abundance) 537 ($M^+ + 1$, 39) , 536 (M^+, 100), 215 (8), 187 (9), 179 (23), 178 (20), 165 (12), 163 (11), 129 (14), 105 (18), 77 (16). Anal. Calcd for $C_{37}H_{28}O_4$: C, 82.82; H, 5.26. Found: C, 82.57; H, 5.38.

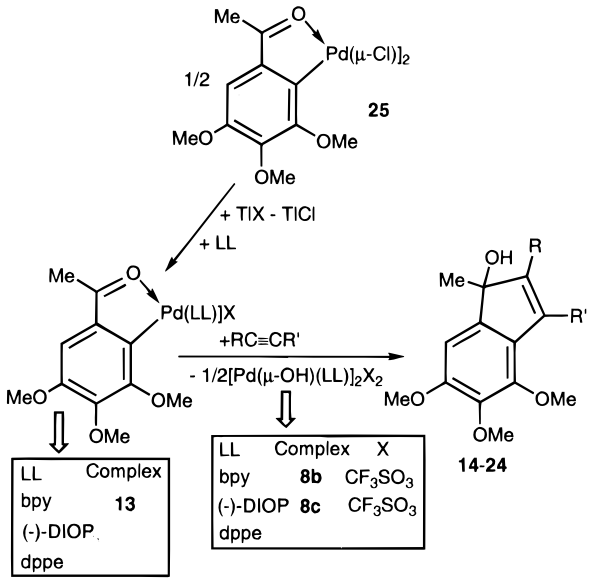
Synthesis of the Indenol 14. 2-Iodo-3,4,5-trimethoxyacetophenone (150 mg, 0.45 mmol), PhC≡CPh (168 mg, 0.94 mmol), $Pd(OAc)_2$ (5 mg, 0.024 mmol), PPh_3 (12 mg, 0.048 mmol), and NEt_3 (0.17 cm^3, 1.22 mmol) were mixed in nitromethane (6 cm^3) and heated to 100 °C in a Carius tube for 4 h. The mixture was evaporated and the residue extracted with Et_2O (3 × 10 cm^3). The combined extracts were filtered through Celite and evaporated to dryness. The residue was washed with pentane and chromatographed over silica gel, with a hexane/Et_2O (1:1) solution as eluent. A colorless band (R_f *ca.* 0.2) was collected, giving **14**. Yield: 38 mg, 22%.

Results

Reactions of (*o*-Formylaryl)palladium Complexes with Alkynes. The anionic complex $(PhCH_2PPh_3)_2[Pd_2(R^1)_2Cl_2(\mu\text{-}Cl)_2]$ (**1**; R^1 = 6-formyl-2,3,4-trimethoxyphenyl) reacts at room temperature with PhC≡CPh (1:10), giving metallic palladium, the indenone **2** (isolated 77%), $(PhCH_2PPh_3)Cl$, and a small amount of the indenol **3** (**2**:**3** = 6.5) (Scheme 1). **1** reacts with $MeO_2CC{\equiv}CCO_2Me$ (1:2) at room temperature to give traces of metallic palladium and a complex mixture of compounds. When a 1:2.2 mixture of the same reagents in acetonitrile is refluxed, metallic palladium and a complex mixture was obtained. From this mixture, the indenone **4** was isolated in low yield (17%). A different behavior was observed in the reaction with $Me_3SiC{\equiv}CSiMe_3$ (1:6), which gave the alkyne **5** (42%). The reaction of **1** with other alkynes (MeC≡CMe, PhC≡CH, $PhC{\equiv}CCO_2Me$) gave complex mixtures that could not be separated.

When PhC≡CPh was reacted with the neutral complex $[Pd(R^1)Cl(bpy)]$ (**6**; bpy = 2,2′-bipyridine) (see Scheme 1) in the presence of $Ag(ClO_4)$ (4:1:1) or with the cationic $[Pd(R^1)(NCMe)(bpy)]ClO_4$ (**7**; 2:1), the hydroxo dimer **8a** and the indenol **3** were formed (73 or 67%, respectively). In these reactions no other organic compound was detected. The complex $[Pd(R^2)(NCMe)(bpy)]ClO_4$ (**9**; R^2 = 2-formyl-3,4,5-trimethoxyphenyl) behaves similarly to its isomer **7**, reacting with PhC≡CPh (1:2) to give **8a** and the indenol **10** (96%). When complex **7** or **9** was reacted at 80 °C with PhC≡CPh under anhydrous conditions, metallic palladium and the indenone **2** (64%) or **11** (38%), respectively, was obtained instead (Scheme 1). Other alkynes (MeC≡CMe, PhC≡CH, $MeO_2CC{\equiv}CCO_2Me$, $Me_3SiC{\equiv}CSiMe_3$) react with **7** or **9** to give complex mixtures that could not be separated. The neutral complex $[Pd(\eta^2\text{-}R^2)(\mu\text{-}Cl)]_2$ (**12**)

Scheme 2

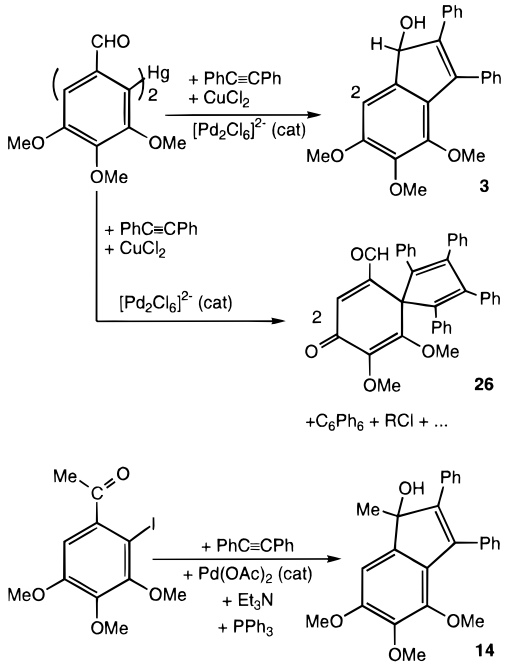


LL	Compound	R	R'	a:b
bpy	**14**	Ph	Ph	-
bpy	**15**	To	To	-
bpy	**16**	CO_2Me	CO_2Me	-
bpy	**17**	Me	Me	-
bpy	**18**	Et	Et	-
bpy	**19a (b)**	CO_2Et (Ph)	Ph (CO_2Et)	1:1.3
bpy	**20a (b)**	^{t}Bu (Me)	Me (^{t}Bu)	1:1
bpy	**21a (b)**	Ph ($C_6H_4NO_2$-4)	$C_6H_4NO_2$-4 (Ph)	1:2
bpy	**22a (b)**	Ph (C_6H_4OMe-4)	C_6H_4OMe-4 (Ph)	2:1
bpy	**23a**	Ph	Me	-
bpy	**24**	H	^{t}Bu	-
(-)-DIOP	**14**	Ph	Ph	-
(-)-DIOP	**15**	To	To	-
(-)-DIOP	**23a (b)**	Ph (Me)	Me (Ph)	1:10
dppe	**23a (b)**	Ph (Me)	Me (Ph)	7:1

reacts with PhC≡CPh (1:5 or 1:2) to give metallic palladium, a 1:1 mixture of the indenol **10** and the indenone **11**, and traces of R^2H (Scheme 1).

Reactions of (*o*-Acetylaryl)palladium Complexes with Alkynes. Reactions of [Pd(η^2-R^3)(bpy)](CF_3SO_3) (**13**; R^3 = 6-acetyl-2,3,4-trimethoxyphenyl) with alkynes (*ca.* 1:1) gave moderate to high yields of 1-methylindenols (Scheme 2) and the hydroxo complex **8b**. Using an excess of alkyne gave the same result. With symmetrical alkynes RC≡CR (R = Ph, 4-tolyl, CO_2Me, Me, Et) 1-methylindenols **14**−**18** were obtained. The reactions of **13** with several unsymmetrical alkynes can be classified in the following groups. (i) Little or no regioselectivity is found in reactions with PhC≡CCO_2Et or MeC≡C^{t}Bu, giving **19a** and **19b** (1:1.3) or **20a** and **20b** (1:1), respectively. (ii) Reactions with PhC≡CC_6H_4-NO_2-4 or PhC≡CC_6H_4OMe-4 are of low regioselectivity, giving isomeric mixtures of **21a** and **21b** (1:2) or **22a** and **22b** (2:1), respectively. (iii) The reactions with PhC≡CMe or ^{t}BuC≡CH are regioselective, giving **23a** or **24**, respectively. The highly regioselective synthesis

Scheme 3



of other 1-methylindenols has been reported by reacting ortho-manganated acetophenone with different alkynes.[12a]

Since the carbon 1 of these indenols is chiral, we have tried these reactions to make them enantioselective. Thus, we have started from the complex [Pd(η^2-R^3)(μ-Cl)]$_2$ (**25**) and reacted it with (−)-DIOP in the presence of Tl(CF_3SO_3), causing the *in situ* formation of a cyclopalladated DIOP complex (Scheme 2). Treatment of these solutions with alkynes gave [Pd(μ-OH)(DIOP)]$_2$-(CF_3SO_3)$_2$ (**8b**) and the corresponding indenols. Thus, the reactions with PhC≡CPh or ToC≡CTo (To = C_6H_4-Me-4) gave the indenols **14** and **15**, respectively, as mixtures of enantiomers with low enantiomeric excesses (see Experimental Section). The reaction with PhC≡CMe gives a very low enantiomeric excess, but surprisingly, the regioselectivity is dramatically changed (**23a**:**23b** = 1:10) compared to that observed with the bpy complex **13**, which gave only **23a**. However, a similar test with 1,2-bis(diphenylphosphino)ethane inverts the regioselectivity again, giving **23a** and **23b** in a 7:1 molar ratio.

Catalytic Processes. We have attempted the synthesis of some of the above organic products through palladium-catalyzed processes following well-established methods.[2a,9,25] For example, the reaction of [Hg-(R^1)$_2$] with PhC≡CPh and $CuCl_2$ (as reoxidant) in the molar ratio 1:6:2, in acetone, in the presence of Q_2[Pd_2-Cl_6] (0.05) (Q = Me_4N, $PhCH_2PPh_3$), gives the indenol **3** in a 62% yield with respect to the group R (Scheme 3). When a similar reaction (Q = $PhCH_2PPh_3$) is carried out in freshly distilled acetone, under nitrogen, the spirocyclic compound **26** is obtained (17% yield) along with C_6Ph_6 and RCl. This is the only example known in which a formylaryl complex gives a product of the diinsertion of the alkyne. We have previously reported

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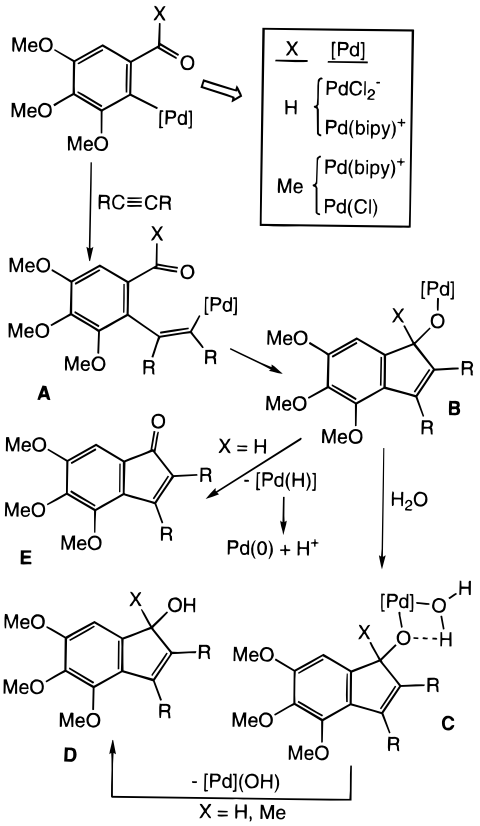
Scheme 4



the synthesis of similar spiro compounds starting from *o*-acetylaryl complexes.[18] The reaction yielding **3** can also be made catalytic in copper using oxygen as the reoxidant (52% yield). **14** could be obtained (only 22% yield) from the iodoarene using palladium acetate (1:0.05) as the catalyst in the presence of Et_3N and PPh_3 (1:1:0.1) in DMF (4 h, 100 °C).

Discussion

The first conclusion we can infer from the above results is that reactions of the studied arylpalladium complexes with different alkynes are very dependent on the nature of the complex. Thus, while the (*o*-formylaryl)palladium complexes **1**, **7**, **9**, and **12** give indenones or indenols (Scheme 1), the *o*-acetylaryl complex **13** or **25** leads to indenols (Scheme 2) or, respectively, spiro compounds or benzofulvenes.[18] The formation of indenols or indenones is usually accompanied by the formation of a hydroxopalladium complex such as **8a** or Pd(0), respectively. If precautions against the presence of moisture are not taken, the result also depends on the nature of the complex. Thus, the anionic complex **1** gives mainly indenones **2** and **4**, while the cationic complexes **7** and **9** or that resulting from the reaction of **6** with $Ag(ClO_4)$ give indenols **3** and **10** (Scheme 1).

We propose the pathway given in Scheme 4 to rationalize the formation of indenols and indenones. First, an alkyne molecule inserts into the Pd−C bond to give the alkenyl derivative **A**. Monoinserted palladium compounds of this type have been isolated from reactions of arylpalladium complexes with alkynes, and their intermediacy to organic compounds is also well documented.[26] Addition of the Pd−C bond across the carbonyl group gives the (indelato)palladium complex **B**. In the palladium-catalyzed formation of indenones from *o*-halobenzaldehydes and alkynes[2a] or methyl acrylate,[27] a pathway involving the oxidative addition of the C−H bond of the formyl group to give a hydrido−Pd(IV) intermediate has been suggested. However, there does not appear to be any precedent for this oxidative addition in palladium chemistry, whereas indenolato complexes related to **B** have been isolated by reacting the cyclopalladated phenyl 2-pyridyl ketone complex with alkynes.[28] From the intermediate **B**, two different reaction pathways are possible. A hydrolytic process, through the aquo complex **C**, gives indenols **D** and a hydroxo complex (**8a** in our case), or a β-elimination process leads to indenones **E** and a hydrido−palladium complex that decomposes to Pd(0). This route seems only to be available for formylaryl complexes. In the well-known processes of oxidation of alcohols to carbonyl compounds using palladium complexes,[29] the formation of alkoxo intermediates, such as **B**, has also been proposed, giving a carbonyl compound and a hydrido−palladium complex which decomposes to give Pd(0) and H^+. In addition, it has also been proposed that some alkoxo complexes of palladium decompose similarly through a β-elimination process.[30]

Formation of indenols is favored when the formylaryl complexes are cationic, because they more easily coordinate water to give the intermediate **C**. In fact, under normal conditions, PhC≡CPh reacts with the anionic complex **1**, giving a molar ratio indenol **3**:indenone **2** of 0.15; with the neutral complex **12** the ratio indenol **10**:indenone **11** is 1, while the cationic complex **7** or **9** gives indenol **3** or **10**, respectively, and only traces of indenone **2** or **11**, respectively, were detected in the crude reaction mixture. In addition, formation of indenone **2** or **11**, instead of indenol **3** or **10**, when cationic complex **7** or **9**, respectively**,** reacts with PhC≡CPh under anhydrous conditions also supports our proposal.

We have also studied the effect of solvent, added water and the amount of the alkyne in the reaction between PhC≡CPh and **1**. The effect of the solvent is less important than the nature of the complex, because the molar ratio indenol **3**:indenone **2** is 1 when the solvent is acetone (0.15 in CH_2Cl_2). However, the presence of adventitious water in acetone could partially be responsible for the increase in indenol according to our proposal. In fact, if a 5:1 (v/v) mixture of acetone/water is used as solvent instead of dichloromethane, the molar ratio indenol **3**:indenone **2** increases by a factor of 26. The reaction between **1** and PhC≡CPh gives the indenol **3** instead of the **2**:**3** mixture found in the stoichiometric reaction (see Scheme 1) because the ratio H_2O:Pd in the catalytic process is much greater than in the stoichiometric reaction. The increase in the molar ratio PhC≡CPh:**1** from 2 to 10 has no effect in dichloromethane, while in acetone the molar ratio indenol **3**:indenone **2** decreases from 1 to 0.3. These results suggest that an excess of alkyne partially suppresses coordination of the adventitious water in acetone.

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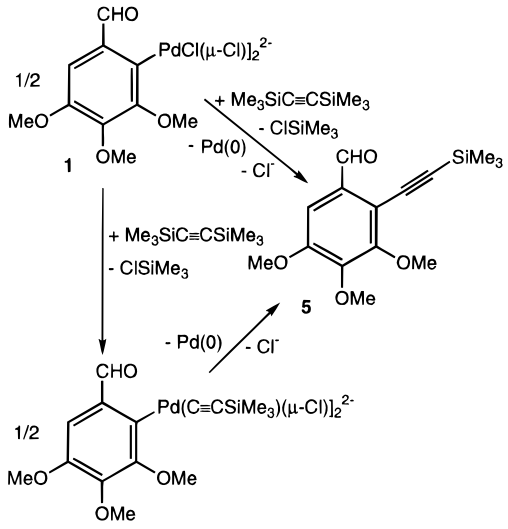
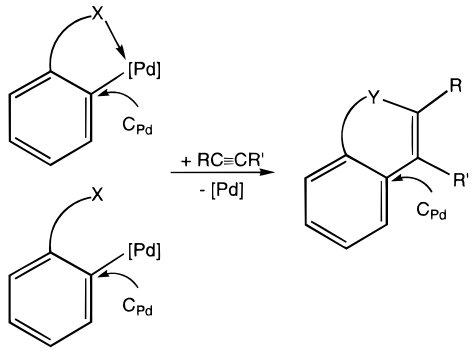
Scheme 5



Scheme 6



We have postulated an acid-catalyzed dehydration of 1-methyl-3-alkylindenols such as **17**, **18**, and **23a** in the formation of benzofulvenes from the corresponding alkynes and complex **25**.[18] Such indenols were not isolated then, according to this assumption, because HCl is also formed in the process. Its isolation now allows us to confirm that addition of a catalytic amount of CF_3SO_3H to $CDCl_3$ or CH_2Cl_2 solutions of **17**, **18**, and **23a** gives quantitatively (by NMR spectroscopy or TLC) the corresponding benzofulvenes.

It is reasonable to assume formation of the alkyne **5** through an intermediate aryl alkynylide complex such as is shown in Scheme 5. A coupling process would give **5**. This process is unprecedented, although some alkynes have been prepared by reacting ((trimethylsilyl)alkyl)- or ((trimethylsilyl)aryl)alkynes with aryl iodides in the presence of catalytic amounts of palladium compounds.[31]

The reactions of **13** with unsymmetrical alkynes are of three regioselective types. We observe no regioselectivity with PhC≡CCO_2Et and ^{t}BuC≡CMe, only moderate regioselectivity with diarylalkynes, and complete regioselectivity with PhC≡CMe and ^{t}BuC≡CH (Scheme 2). This behavior of PhC≡CCO_2Et has only previously been found in a few cases.[32] Usually, reactions of cyclopalladated compounds with alkynes RC≡CR′, R being Ph and R′ an electron-withdrawing substituent

Table 1

R[a]	R′[a]	selec[b]	ref
Ph	CO_2Et	r	25c, 26a, 33a,b,d
Ph	CO_2Et	r, p	25a, 28
Me	CO_2Et	r	28
Ph	CHO	r	25a, 28, 33a
Ph	C(O)Me	r	33a
Ph	$SO_2C_6H_4$Me-4	r	28
Si(^{i}Pr)$_3$	Ph	r	25a
$SiMe_3$	Ph	r	2a, 25a
C(OH)Me_2	Ph	r	2a, 25a
^{t}Bu	Ph	r	2a
$C_6H_4NO_2$-4	Ph	p	this work
C_6H_4OMe-4	Ph	p	2a, 25c
Ph	C_6H_4Me-4	n	25c
Ph	C_6H_4OMe-4	n	2a, 25c
Ph	C_6H_4OMe-4	p	this work
Ph	$C_6H_4CF_3$-4	n	25c
alkyl, aryl	H	r	37[c]
Ph	Me	r	25a−c, 33b, this work
Ph	Me	n	2a
^{t}Bu	Me	r	2a, 18, 25a,b, 28, 35a
c-C_6H_{11}	Me	r	25b
Si(^{i}Pr)$_3$	Me	r	25a
$SiMe_3$	Me	r	25b
CH_2OH	Me	r	25b
C(OH)(C_6H_{12})	Et	r	25a,b
$SiMe_3$	c-C_6H_9	r	2a
$SiMe_3$, $SiMe_2{}^t$Bu	$HOCH_2$	r	25b, 31b
CMe_2OH	CH_2dCMe	r	25b

[a] The R and R′ positions are indicated in Scheme 6. [b] Legend: r = regioselective; p = partially regioselective (the most abundant regioisomer is indicated); n = nonregioselective. [c] Although the authors propose a mechanism not involving an insertion step, this possibility cannot be discarded.

such as CO_2R, CHO, or *p*-$ToSO_2$, give monoinserted products with complete regioselectivity toward the regioisomer in which the electron-withdrawing substituent becomes attached adjacent to the carbon atom originally bonded to Pd (C_{Pd}).[26a,28,33] This could indicate an electronic control of these reactions, since the Ph and CO_2R groups are of comparable size. There are a few exceptions to this rule, which have the opposite regioselectivity.[34]

When R and R′ are electronically similar but very different sterically, as in the case of ^{t}BuC≡CMe or ^{t}BuC≡CH, it has been proposed that the result depends on the strength of the chelate which the aryl group forms with palladium.[35a] If the complex has a weak chelating group, the regioisomer expected according to this model is that in which the largest substituent becomes attached adjacent to C_{Pd} (R′ in Scheme 6). The only example given to illustrate this behavior is the reaction of a cyclopalladated complex of 2-(dimethylamino)biphenyl.[32,35a] In our case, as the C,O-chelate in **13** must be even weaker than the above C,N group, the expected methylindenols from ^{t}BuC≡CMe or ^{t}BuC≡CH should be those with R′ = ^{t}Bu (see Scheme 2). However, although ^{t}BuC≡CH gives the expected regioisomer, the reaction with ^{t}BuC≡CMe is unregioselective. Additionally, in palladium-catalyzed annulation of this type of alkyne with *o*-iodo or *o*-bromo derivatives of phenols, methyl benzoate,[25a] benzaldehyde,[2a] or anilines,[25b] the

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Table 2

R[a]	R¢ [a]	selec[b]	ref	aryl group
^{t}Bu	Me	p	35a	2-((*tert*-butylthio)methyl)phenyl
Me	^{t}Bu	n	this work	*o*-acetylaryl
H	^{t}Bu	r	this work	*o*-acetylaryl
Me	^{t}Bu	r	35a	(dimethylamino)biphenyl
H	Ph	r	1	*o*-styrylaryl
CHO	Ph	n	32	(dimethylamino)biphenyl
CO_2Et	Ph	n	this work, 32	*o*-acetylaryl, 2-(2-(methylthio)- or 2-(dimethylamino)biphenyl)
CO_2Et	Ph	r	34	2-arylazoaryl
Ph	$CH(OEt)_2$	r	34	2-arylazoaryl
Me	Ph	n	2a	2-formylaryl

[a] The R and R′ positions are indicated in Scheme 6. [b] Legend: r = regioselective; p = partially regioselective (the most abundant regioisomer is indicated); n = nonregioselective.

regioisomer obtained is that with the less bulky substituent as R′. Bearing in mind that the intermediate aryl complexes would also be weakly chelating or nonchelating, this result contradicts the above model. The behavior of ^{t}BuC≡CH is contrary to that found in the reaction of RC≡CH (R = ^{n}Bu, $^nC_6H_{11}$, $SiMe_3$) with ortho-manganated benzophenone.[12a]

Table 1 summarizes data from the literature and this work on the regioselectivity of the insertion of alkynes into Pd−aryl bonds as an exclusive function of the nature of the alkyne substituents. The R′ group is that placed next to C_{Pd} (see Scheme 6) and is usually the most electron withdrawing and/or less bulky group. The following scale gives the tendency of a group to be in the R′ position:

$$CO_2Et \approx CHO \approx C(O)Me \approx SO_2C_6H_4Me\text{-}4 \geq H > Me \approx Et > aryl > {}^tBu \approx SiR_3$$

The differences in electron-withdrawing abilities of different aryl groups (such as those studied here) seem not to be enough to determine a clear regioselectivity. Reactions of arylpalladium complexes with diarylalkynes, such as PhC≡C$C_6H_4NO_2$-4 and PhC≡CC_6H_4-OMe-4, have been shown to be nonregioselective [25c,35] or, as in our case, scarcely selective.[18] In this case, there are examples in which the most electron withdrawing aryl group is placed in the R′ position, as expected,[2a,25c] but there are also examples to the contrary, as has already been mentioned. Consequently, we think that when two groups have similar tendencies to be in the R′ position, according to the above scale, other factors must be responsible for any observed regioselectivity.

The case of the complete regioselectivity of PhC≡CMe has many precedents, [25a−c,33b,36] and follows the above rule. In some cases no regioselectivity is observed.[2a] As the data in Table 1 are from very different arylpalladium complexes, in particular, aryl groups with different capacities to chelate to palladium, it can be concluded that regioselectivity is mainly determined by the nature of the alkyne.

Table 2 gives some exceptions to the above-stated empirical rule. The exceptions could be due to the influence of other factors. Most of the aryl groups implicated in these exceptional cases are weakly chelating. Therefore, they follow the Pfeffer model (see above).[35a] It is then possible to assume that weakly chelating aryl groups can induce the unusual insertion of alkynes into the aryl−palladium bond, although this condition is not sufficient to determine such behavior. The change of selectivity when in $[Pd\{C_6(C(O)Me)\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}(LL)]^+$ the ligand LL is changed from bpy or 1,2-bis(diphenylphosphino)ethane to (−)-DIOP (Scheme 2) proves that steric congestion around the metal center can also influence the regioselectivity of the insertion reaction.

Conclusions

We have studied the reactivity of *o*-carbonyl-functionalized arylpalladium complexes with alkynes, obtaining two indenones and a wide range of indenols. We have also shown the influence of the nature of the complex, of the aryl group, and of the presence of water on the nature of the reaction products. Indenols are preferentially formed when cationic *o*-formylaryl complexes are used as starting materials in the presence of moisture or added water. Neutral or anionic complexes tend to give mixtures of indenol and indenones, depending on the degree of moisture present in the solvent. Indenones are formed under anhydrous conditions or from an anionic complex. *o*-Acetylaryl complexes always give indenols. We have also studied the regiochemistry of these reactions using unsymmetrical alkynes. We believe that in most insertion reactions of an alkyne into an aryl−palladium bond, the regioisomer obtained depends on the nature of the alkyne. The regioisomer obtained is that which has the most electron withdrawing and/or the least bulky substituent placed next to the carbon atom originally bonded to Pd. No regioselectivity can be found when the substituents have similar tendencies to occupy one or the other position. Exceptions to this rule, mostly from this work, could be due to other factors: the chelating ability of the aryl group, the nature of other ligands in the complex, etc. More work remains to be done to justify the above rule and its exceptions. Most attempts to obtain indenols or indenones catalytically have failed.

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