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Palladium-Assisted Formation of Carbon−Carbon Bonds. 5.[1] Reactions of (*o*-Styrylaryl)palladium Complexes with Alkynes. Synthesis of Palladium Complexes with Highly Functionalized Indenyl Ligands. Crystal and Molecular Structures of (1-Benzyl-2,3-diphenyl-5,6,7-trimethoxyindenyl)- and (1-Benzyl-3-phenyl-5,6,7-trimethoxyindenyl)palladium(II) Complexes

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The reactions of [Pd(*E*-R)Cl(tmeda)] [R = C_6H(*E*-CH═CHPh)-6-$(OMe)_3$-2,3,4; tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine] with $Tl(CF_3SO_3)$ and CH≡CH, PhC≡CPh, or PhC≡CH selectively give compounds [Pd(η-Ind)(tmeda)]CF_3SO_3 [Ind = 1-benzyl-5,6,7-trimethoxyindenyl (**2**), 1-benzyl-2,3-diphenyl-5,6,7-trimethoxyindenyl (**3**), 1-benzyl-3-phenyl-5,6,7-trimethoxyindenyl (**4**)]. When a mixture of [Pd(*E*-R)Cl(bipy)] (bipy = 2,2′-bipyridine) and [Pd(*Z*-R)Cl(bipy)] is reacted with $Tl(CF_3SO_3)$ and MeC≡CMe, the complex [Pd(η-Ind)(bipy)]CF_3SO_3 [1-benzyl-2,3-dimethyl-5,6,7-trimethoxyindenyl (**5**)] is obtained. The structures of **3** and **4** have been determined by X-ray studies at 203 and 173 K, respectively. According to the structural data for **3** and **4**, the hapticity of the indenyl ligands is intermediate between η^3- and η^5-coordination.

Introduction

It is well-known that transition metal indenyl complexes display a higher reactivity in stoichiometric and catalytic reactions than their cyclopentadienyl analogues.[2−4] Very interesting polymerization catalysts have been described that involve *ansa* metallocenes containing indenyl groups.[5] In addition, some rhodium, iridium, and early transition metal catalysts with substituted indenyl ligands show increased activity and lifetimes compared with the corresponding unsubstituted derivatives.[6−8] However, apart from the parent ligand C_9H_7, very few substituted indenyl complexes are known, most of them being alkyl-, aryl-,[2,5−13] halo-,[14,15] or ferrocenylindenyl derivatives.[16] Furthermore, to the best of our knowledge, [$Pd_2(\mu$-η^3-$C_9H_7)_2(CNR)_2$] (R = Bu^t, $C_6H_3Me_2$-2,6, $C_6H_2Me_3$-2,4,6, and $C_6H_2Bu^t_3$-2,4,6)[17] and [$Pd_2(\eta^3$-$C_9H_7)_2(\mu$-$Cl)_2$][18] are the only known indenylpalladium complexes. Several impure (methyl- or (phenylindenyl)palladium derivatives, prepared from the reaction of cyclopropenes and [$PdCl_2(PhCN)_2$], have been reported only in a preliminary communication.[19]

The reactivity of arylpalladium compounds with alkynes constitutes a topic of current interest.[20] These reactions usually involve insertion of 1, 2, or 3 alkyne molecules into the carbon−palladium bond giving new species, which may be stable and isolable or can undergo

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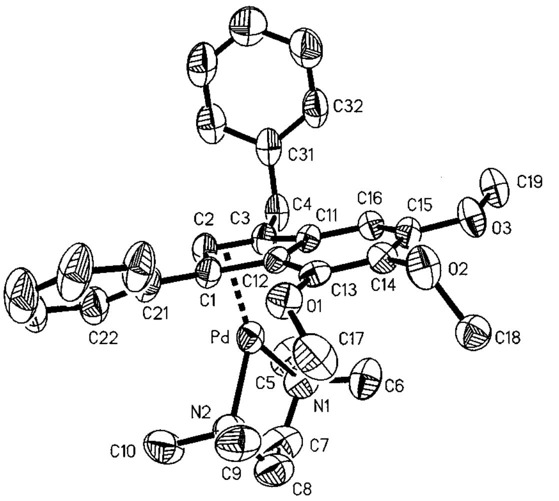

Figure 1. Crystal structure of **3**. Selected bond distances (Å) and angles (deg) not included in the text: Pd−N(1) 2.147(4), Pd−N(2) 2.145(4), C(1)−C(2) 1.434(6), C(1)−C(12) 1.491(5), C(2)−C(3) 1.422(6), C(3)−C(11) 1.479(6), C(11)−C(12) 1.424(6), C(12)−C(13) 1.392(6), C(13)−C(14) 1.395(6), C(14)−C(15) 1.396(6), C(15)−C(16) 1.382(6), N(2)−Pd−N(1) 84.3(2), C(2)−C(1)−C(12) 107.5(4), C(3)−C(2)−C(1) 108.1(4), C(2)−C(3)−C(11) 107.8(4), C(12)−C(11)−C(3) 107.7(4), C(11)−C(12)−C(1) 107.0(4).

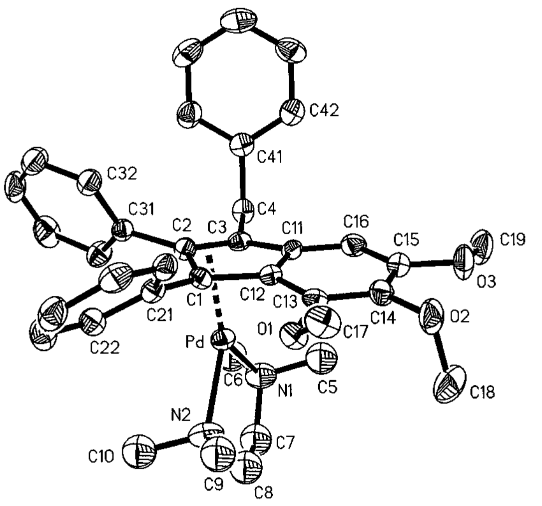

Figure 2. Crystal structure of **4**. Selected bond distances (Å) and angles (deg) not included in the text: Pd−N(1) 2.126(5), Pd−N(2) 2.132(5), C(1)−C(2) 1.415(7), C(1)−C(12) 1.500(6), C(2)−C(3) 1.407(7), C(3)−C(11) 1.482(6), C(11)−C(12) 1.407(6), C(12)−C(13) 1.409(6), C(13)−C(14) 1.398(7), C(14)−O(2) 1.375(5), C(14)−C(15) 1.396(7), C(15)−C(16) 1.386(6); N(1)−Pd−N(2) 84.1(2), C(2)−C(1)−C(12) 105.8(4), C(3)−C(2)−C(1) 110.3(4), C(2)−C(3)−C(11) 106.3(4), C(12)−C(11)−C(3) 108.1(4), C(11)−C(12)−C(1) 107.4(4).

a depalladation process to give organic compounds.[20,21] The subject of this article is the reactivity of some (*o*-styrylaryl)palladium complexes with alkynes, leading to indenyl complexes.

Experimental Section

Infrared spectra, ^{1}H and ^{13}C NMR spectra, C, H, N, and S analyses, conductance measurements, melting point determinations, and purification of solvents were carried out as described elsewhere.[21] Some ^{13}C NMR signals were assigned with the help of the DEPT technique. The carbon analyses for complexes **2**−**4** give low values (−2 to −3% absolute error) despite repeated recrystallizations. However, good analyses for H, N, and S as well as their NMR spectra prove they are pure compounds. We believe this problem is associated with the presence of triflate in these compounds. Complexes **1a**,**b** were prepared as previously described.[22]

Reaction of 1a with HC≡CH. Synthesis of 2. Acetylene was bubbled for 5 min through a suspension of **1a** (120 mg, 0.228 mmol) and $Tl(CF_3SO_3)$ (81 mg, 0.228 mmol) in CH_2Cl_2 (10 cm^3). The brown suspension was stirred for 20 h and filtered over anhydrous $MgSO_4$. The solution was concentrated to 1 cm^3, and diethyl ether was added to precipitate **2** as a brown solid. Yield: 88 mg, 58%. Mp: 145−147 °C. Λ_M (acetone): 104 Ω^{-1} cm^2 mol^{-1}. NMR: ^{1}H-NMR (200 MHz, $CDCl_3$, ppm) 7.20−7.40 (m, C_6H_5, 5 H), 6.71 (d, indenyl-CH, 1 H, ^3J = 3 Hz), 6.44 (s, Aryl-H, 1 H), 5.71 (d, indenyl-CH, 1 H, ^3J = 3 Hz), 3.92, 3.81 and 3.79 (s, MeO, 3 H), 3.36 (d, C*H*$_2$Ph, 1 H, ^2J = 15 Hz), 3.27 (d, C*H*$_2$Ph, 1 H, ^2J = 15 Hz), 2.55−2.85 (m, CH_2CH_2, 4 H), 2.87, 2.77, 2.75, and 2.60 (s, MeN, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$, ppm) 154.34, 144.79, 141.29, 136.14, and 133.57 (C-aryl), 128.79 and 128.23 (*o*,*m*-C_6H_5), 126.97 (*p*-C_6H_5), 122.32 (C-aryl), 109.66 (indenyl-CH), 96.57 (R-*C*H), 93.74 (indenyl-C), 74.48 (indenyl-CH), 61.73 (*C*H$_2$CH$_2$), 61.17 and 61.10 (MeO), 60.73 (CH$_2$*C*H$_2$), 56.52 (MeO), 54.32, 52.73, 51.61, and 51.39 (MeN), 32.80 (Ph*C*H$_2$). Anal. Calcd for $C_{26}H_{35}F_3N_2O_6PdS$: C, 46.82; H, 5.29; N, 4.20; S, 4.81. Found: C, 45.44; H, 5.51; N, 4.58; S, 4.96.

Reaction of 1a with PhC≡CPh. Synthesis of 3. Brown **3** was similarly prepared from diphenylacetylene (68 mg, 0.380 mmol), **1a** (100 mg, 0.190 mmol), and $Tl(CF_3SO_3)$ (67 mg, 0.190 mmol). Yield: 106 mg, 56%. Mp: 158−159 °C. Λ_M (acetone): 109 Ω^{-1} cm^2 mol^{-1}. NMR: ^{1}H-NMR (200 MHz, $CDCl_3$, ppm) 7.25−7.35 (m, C_6H_5, 6 H), 7.05−7.20 (m, C_6H_5, 7 H), 6.85−6.93 (m, C_6H_5, 2 H), 6.57 (s, R-H, 1 H), 3.91, 3.85, and 3.82 (s, MeO, 3 H), 3.31 (s, C*H*$_2$Ph, 2 H), 2.60−3.00 (m, CH_2-CH_2, 4 H), 3.01, 2.73, 2.63, and 2.40 (s, MeN, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$, ppm) 154.49, 145.91, 142.23, 134.91, 132.91, 131.58, and 131.56 (C-aryl), 131.04 (CH), 129.84 (C-aryl), 128.61, 128.40, 128.37, 128.25, 128.06, 127.13, 126.68 (CH-aryl), 118.90, 96.88, and 94.95 (indenyl-C), 90.86 (CH-aryl), 62.14 and 61.38 (*C*H$_2$*C*H$_2$), 60.82, 60.22, and 56.54 (MeO), 53.07, 52.75, 50.72, and 50.40 (MeN), 30.91 (Ph*C*H$_2$). Anal. Calcd for $C_{38}H_{43}F_3N_2O_6PdS$: C, 55.71; H, 5.29; N, 3.42; S, 3.91. Found: C, 54.50; H, 5.41; N, 3.60; S, 3.83. Single crystals of **3** were obtained by liquid diffusion of diethyl ether into a solution of **3** in dichloromethane.

X-ray Structure Determination of 3.2CH$_2$Cl$_2$. *Crystal data*: $C_{40}H_{47}Cl_4F_3N_2O_6PdS$, monoclinic, $P2_1/c$, a = 18.301(2) Å, b = 11.335(2) Å, c = 21.351(3) Å, β = 96.380(8)°, V = 4401.5 Å^3, Z = 4, D_x = 1.493 Mg m^{-3}, λ(Mo *K*α) = 0.710 73 Å, μ = 0.8 mm^{-1}. *Data collection*: A dichroic brown/violet plate 0.75 × 0.4 × 0.1 mm was mounted on a Siemens P4 diffractometer fitted with an LT-2 low-temperature device. A total of 10 228 intensities were recorded at 203 K to $2\theta_{max}$ 50°. After absorption corrections (ψ-scans), 7743 unique reflections were used for all calculations. *Structure refinement* was on F^2 (program SHELXL-93, G. M. Sheldrick, Univ. of Göttingen) with riding H atoms; the carbon atoms of the tmeda ligand are disordered over two sites $wR(F^2) = 0.098$, and conventional $R(F) = 0.047$ for 502 parameters and 510 restraints (S = 0.81; maximum $\Delta\rho$ = 0.66 e Å^{-3}).

Reaction of 1a with PhC≡CH. Synthesis of 4. Dark brown **4** was similarly prepared from phenylacetylene (44 mg, 0.431 mmol), **1a** (100 mg, 0.190 mmol), and $Tl(CF_3SO_3)$ (67 mg, 0.190 mmol). Yield: 117 mg, 83%. Mp: 96−98 °C. Λ_M (acetone): 115 Ω^{-1} cm^2 mol^{-1}. NMR: ^{1}H-NMR (200 MHz, $CDCl_3$, ppm) 7.85−7.95 (m, C_6H_5, 2 H), 7.20−7.50 (m, C_6H_5, 8

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Scheme 1. Suggested Pathway (Dashed Arrows) for the Synthesis of 2−5 (LL = tmeda, LL′ = bipy)

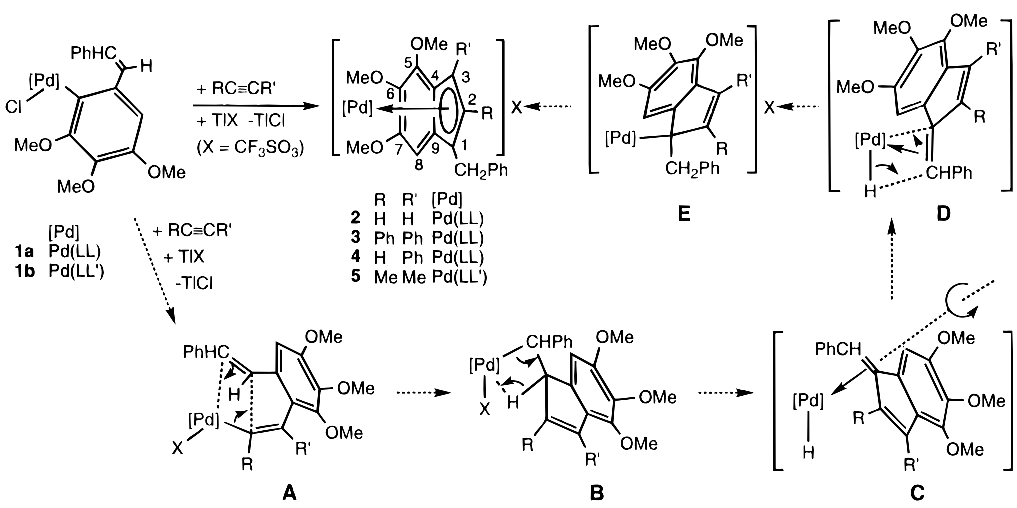

Table 1. Crystal Data and Structure Refinement for 3 and 4

empirical formula	$C_{40}H_{47}Cl_4F_3N_2O_6PdS$	$C_{33}H_{40}Cl_3F_3N_2O_6PdS$
fw	989.06	862.48
temp, K	203	173
wavelength, Å	0.710 73	0.710 73
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a, Å	18.301(2)	14.836(2)
b, Å	11.335(2)	12.150(2)
c, Å	21.351(3)	20.906(3)
β, deg	96.380(8)	101.58(1)
V, Å^3	4401.5(11)	3691.7(10)
D_{calc}, Mg/m^3	1.493	1.552
abs coef, mm^{-1}	0.771	0.836
F(000)	2024	1760
cryst size, mm	0.75 × 0.40 × 0.10	0.80 × 0.30 × 0.20
θ, deg	3.11−25.00	3.09−25.00
lim ind	$-21 \le h \le 5, 0 \le k \le 13, -25 \le l \le 25$	$-17 \le h \le 1, -14 \le k \le 3, -24 \le l \le 24$
reflcns collcd	10 228	8618
indepdt reflcns	7743 [*R*(int) = 0.0394]	6462 [*R*(int) = 0.0285]
abs corr	*ψ*-scans	*ψ*-scans
max and min transm	0.781 and 0.740	0.869 and 0.735
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2
data/restraints/parameters	7741/510/502	6461/469/463
goodness-of-fit on F^2	0.807	0.894
final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0469$, $wR2 = 0.0855$	$R1 = 0.0471$, $wR2 = 0.0981$
R indices (all data)	$R1 = 0.1072$, $wR2 = 0.0979$	$R1 = 0.1010$, $wR2 = 0.1132$
largest diff peak and hole, e·Å^{-3}	0.665, −0.529	0.468, −0.687

H), 6.75 and 6.56 (s, aryl-H and indenyl-CH, 1 H), 3.86, 3.84, and 3.82 (s, MeO, 3 H), 3.41 (d, C*H*$_2$Ph, 1 H, ^2J = 15 Hz), 3.26 (d, C*H*$_2$Ph, 1 H, ^2J = 15 Hz), 2.65−2.90 (m, CH$_2$-CH$_2$, 4 H), 2.78, 2.67, 2.43, and 2.31 (s, MeN, 3 H); ^{13}C NMR (50 MHz, CDCl$_3$, ppm) 154.48, 146.09, 142.18, 135.93, 135.09, 133.15 (C-aryl), 128.86, 128.76, 128.53, 128.37, 127.05 (CH-aryl), 120.22 (C-aryl), 110.33 (indenyl-C), 96.65 (R-*C*H), 95.06, 91.63 (indenyl-C), 61.64 and 61.21 (*C*H$_2$*C*H$_2$), 60.96, 60.75, and 56.53 (MeO), 51.87, 51.46, 51.32, and 50.16 (MeN), 32.83 (Ph*C*H$_2$). Anal. Calcd for $C_{32}H_{39}F_3N_2O_6PdS$: C, 51.72; H, 5.29; N, 3.77; S, 4.31. Found: C, 50.72; H, 5.41; N, 3.90; S, 4.28. Single crystals of **4** were obtained by liquid diffusion of diethyl ether into a solution of **4** in chloroform.

X-ray Structure Determination of 4·CHCl$_3$: *Crystal data*: $C_{33}H_{40}Cl_3F_3N_2O_6PdS$, monoclinic, $P2_1/c$, a = 14.836(2) Å, b = 12.150(2) Å, c = 20.906(3) Å, β = 101.58(1)°, V = 3691.7 Å^3, Z = 4, D_x = 1.552 Mg m^{-3}, μ = 0.8 mm^{-1}. Other details are as for **3**, with the following differences: dark red prism 0.8 × 0.3 × 0.2 mm, 8618 intensities at 173 K, 6462 unique, $wR(F^2) = 0.113$, conventional $R(F) = 0.047$ for 463 parameters and 469 restraints (S = 0.89; maximum $\Delta\rho$ = 0.47 e Å^{-3}).

Reaction of 1b (*Z/E* Mixture) with MeC≡CMe. Synthesis of 5. Red brown **5** was similarly prepared from 2-butyne (40 mg, 0.740 mmol), **1b** (120 mg, 0.211 mmol), and Tl(CF$_3$SO$_3$) (75 mg, 0.211 mmol). Yield: 125 mg, 81%. Mp: 122−124 °C. Λ_M (acetone): 110 Ω^{-1} cm^2 mol^{-1}. NMR: ^{1}H-NMR (200 MHz, CDCl$_3$, ppm) 8.65−8.72, 8.40−8.50, 8.05−8.25, 7.80−7.90, 7.60−7.70 (m, 8 H, bipy), 7.15−7.45 (m, C$_6$H$_5$, 5 H), 6.62 (s, aryl-H, 1 H), 4.06 (d, C*H*$_2$Ph, 1 H, ^2J = 15 Hz), 3.88, 3.79, and 3.74 (s, MeO, 3 H), 3.47 (d, C*H*$_2$Ph, 1 H, ^2J = 15 Hz), 2.34, 1.82 (s, indenyl-CH$_3$, 3 H); ^{13}C NMR (50 MHz, CDCl$_3$, ppm) 154.51 and 153.11 (C-aryl), 153.00 (CH-aryl), 152.33 (C-aryl), 151.14 (CH-aryl), 145.62 and 141.71 (C-aryl), 140.87 and 140.61 (CH-aryl), 135.13 and 133.28 (C-aryl), 128.72, 128.29, 127.95, 126.97, and 126.80 (CH-aryl), 124.31 (indenyl-C), 124.15 and 123.90 (CH-aryl), 121.69 (C-aryl), 97.21 (R-*C*H), 91.18 and 90.86 (indenyl-C), 60.90, 60.77 and 56.40 (MeO), 30.70 (Ph*C*H$_2$), 12.50 and 12.38 (indenyl-*C*H$_3$). Anal. Calcd for $C_{32}H_{31}F_3N_2O_6PdS$: C, 52.29; H, 4.25; N, 3.81. Found: C, 52.23; H, 4.47; N, 3.91.

Results and Discussion

The complex [Pd(R)Cl(LL)] (**1a**) [R = C$_6$H(*E*-CH=CHPh)-6-(OMe)$_3$-2,3,4; LL = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine; see Scheme 1], which we have prepared through a Wittig reaction,[22] reacts with HC≡CH or PhC≡CPh, in the presence of Tl(CF$_3$SO$_3$), to give the indenylpalladium derivative **2** or **3**, respectively. As far as we are aware, these are the first examples in which an indenyl ligand is formed through such a simple procedure. Also remarkable is the highly functionalized nature of the indenyl ligands. If the reaction is carried out with an unsymmetric alkyne, such as PhC≡CH, the reaction is regioselective and complex **4**, with the phenyl group in the 3 position, is formed as the only isomer. The clean results achieved with terminal alkynes, even with acetylene, in particular contrasts markedly with the usual reactions of arylpalladium complexes with terminal alkynes to give intractable mixtures.[20,23] The reactions with the other alkynes are also very clean as observed in the NMR of the crude products.

A reasonable pathway for the formation of these indenylpalladium complexes is proposed in Scheme 1. The synthesis of monoinserted palladium compounds, such as **A**, when arylpalladium complexes are reacted with alkynes, is well documented.[20] Addition of the Pd−C bond to the alkenyl sustituent, which is a well-known process occurring in palladium-catalyzed cyclization reactions,[24] would give **B**. The successive β-hydride elimination and readdition to give a σ-indenyl complex **E** could occur through hydrido(η^2-benzofulvene)palladium(II) complexes **C** and **D**. Finally, the three-coordinated complex **E** would give the more stable η-indenyl complex.

According to this proposal, the regioselectivity of the reaction with PhC≡CH must be determined in the first step. However, when this type of insertion reaction is regiospecific and the alkyne does not contain electron-withdrawing substituents, the regioisomer obtained is that in which the least bulky substituent is adjacent to the aryl ligand.[21,23,25,26] The same applies to reactions of alkynes with arylmanganese(II) complexes[27] or with haloarenes in the presence of catalytic amounts of palladium complexes.[28] Therefore, the insertion of PhC≡CH follows a contrasting pattern. As far as we are aware, there is only one other reported exception.[26] Further, according to our pathway the result would be the same if the *Z*-isomer of the starting complex were used. In fact, by reaction of a mixture of [Pd(*E*-R)Cl(bipy)] (bipy = 2,2′-bipyridine) and [Pd(*Z*-R)Cl(bipy)] (**1b**) with Tl(CF_3SO_3) and MeC≡CMe, only one complex, [Pd(η-Ind)(bipy)]CF_3SO_3 [1-benzyl-2,3-dimethyl-5,6,7-trimethoxy-indenyl (**5**)], is obtained.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for 3^a

	x	*y*	*z*	*U*(eq)
Pd	2547.9(2)	6352.4(3)	3458.2(2)	26.8(1)
O(1)	819(2)	8004(3)	2365.5(13)	29.1(8)
O(2)	1043(2)	7298(3)	1140.3(14)	44.1(10)
O(3)	1745(2)	5329(3)	930.9(14)	42.3(10)
C(1)	1316(2)	6293(4)	3446(2)	23.6(10)
C(2)	1654(3)	5255(4)	3733(2)	24.4(11)
C(3)	2007(2)	4644(4)	3269(2)	22.9(11)
C(4)	2383(2)	3464(4)	3356(2)	26.5(11)
N(1)	3663(2)	6065(4)	3271(2)	41.5(12)
N(2)	2893(2)	8150(4)	3603(2)	43.6(12)
C(5)	3688(6)	5585(8)	2626(4)	54.2(12)
C(6)	4057(6)	5221(8)	3713(4)	54.2(12)
C(7)	4026(5)	7205(7)	3338(5)	54(2)
C(8)	3601(5)	8196(7)	3320(4)	54(2)
C(9)	2364(5)	9010(8)	3329(5)	54.2(12)
C(10)	3043(5)	8427(8)	4301(3)	54.2(12)
C(5′)	3653(10)	6173(16)	2581(5)	54.2(12)
C(6′)	4034(11)	4970(12)	3503(7)	54.2(12)
C(7′)	4067(8)	7096(12)	3591(8)	54(2)
C(8′)	3689(7)	8159(12)	3608(9)	54(2)
C(9′)	2536(9)	8815(15)	3006(7)	54.2(12)
C(10′)	2650(9)	8842(14)	4113(7)	54.2(12)
C(11)	1732(2)	5140(4)	2646(2)	21.8(10)
C(12)	1325(2)	6178(4)	2751(2)	21.9(10)
C(13)	1103(2)	6918(4)	2245(2)	23.5(10)
C(14)	1256(3)	6589(4)	1644(2)	29.0(12)
C(15)	1634(3)	5546(4)	1550(2)	30.2(12)
C(16)	1887(3)	4821(4)	2048(2)	28.6(11)
C(17)	159(3)	8394(4)	1980(2)	39.6(14)
C(18)	1584(4)	8139(5)	1018(3)	77(2)
C(19)	2235(3)	4416(5)	807(2)	48(2)
C(21)	842(3)	7106(4)	3760(2)	24.0(10)
C(22)	1058(3)	7573(4)	4354(2)	29.9(12)
C(23)	600(3)	8320(4)	4643(2)	39.0(14)
C(24)	−82(3)	8609(5)	4349(2)	40.8(12)
C(25)	−319(3)	8117(4)	3763(2)	34.6(12)
C(26)	143(3)	7368(4)	3479(2)	27.1(11)
C(31)	1632(3)	4861(4)	4397(2)	23.8(10)
C(32)	960(3)	4542(4)	4597(2)	31.4(12)
C(33)	942(3)	4066(4)	5192(2)	40.2(13)
C(34)	1580(3)	3908(4)	5587(2)	43.0(14)
C(35)	2236(3)	4229(4)	5395(2)	42.5(14)
C(36)	2274(3)	4714(4)	4804(2)	33.5(12)
C(41)	1852(3)	2436(4)	3323(2)	27.0(11)
C(42)	1637(3)	1861(4)	2760(2)	33.1(12)
C(43)	1146(3)	928(4)	2729(3)	42.0(14)
C(44)	855(3)	564(4)	3265(3)	48.7(15)
C(45)	1060(3)	1126(4)	3828(3)	46.6(14)
C(46)	1563(3)	2047(4)	3861(2)	37.5(14)
S	6422.8(9)	6432(2)	3040.4(7)	66.1(5)
O(4)	6852(3)	5339(5)	2976(2)	98(2)
O(5)	6826(3)	7509(4)	3089(2)	90(2)
O(6)	5861(2)	6346(5)	3457(2)	79.7(13)
C(99)	5894(4)	6510(6)	2276(3)	59(2)
F(1)	5470(2)	7468(4)	2238(2)	106(2)
F(2)	5469(2)	5589(3)	2162(2)	84.2(13)
F(3)	6332(2)	6566(3)	1819.9(15)	78.2(12)
C(97)	3973(5)	8563(7)	1068(4)	124(3)
Cl(1)	3705(2)	7161(2)	1025.0(13)	170.0(13)
Cl(2)	4282.1(13)	9108(2)	379.2(9)	112.3(8)
C(98)	4223(6)	3031(8)	353(4)	172(5)
Cl(3)	4478(2)	4293(3)	701(2)	172.2(13)
Cl(4)	3636(2)	3058(2)	−285.3(11)	137.2(10)

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

Complexes **3** and **4** have been studied by X-ray diffraction, confirming the proposed structures (see Figures 1 and 2 and Tables 1−3; figure captions give selected bond lengths and angles). In both cases, the distances of Pd to the allylic carbons C(1) [2.253(4), 2.208(5) Å; here and below, data are for **3** and **4**, respectively], C(2) [2.187(5), 2.151(5) Å], and C(3) [2.191(4), 2.212(6) Å] are significantly shorter than those to C(11) [2.585(5), 2.572(5) Å] and C(12) [2.564(4) Å, 2.564(4) Å]. However, these differences are not sufficient to allow the coordination to be described as simply η^3. Thus, the ΔMC values (difference between the average of the metal carbon distances to the "allyl" and "ene" carbons)[14,29] 0.35 and 0.39 Å lie between those expected for an η^3 (0.5−0.9 Å) and those expected for an η^5-

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Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 4[a]

	x	*y*	*z*	*U*(eq)
Pd	3438.3(3)	3695.0(4)	3142.2(2)	41.4(2)
O(1)	1190(2)	3410(3)	4114(2)	45.6(10)
O(3)	2622(3)	6732(3)	5005(2)	50.6(10)
N(1)	4878(3)	3884(5)	3487(2)	54.5(14)
N(2)	3689(3)	2033(4)	3455(2)	53.3(13)
C(1)	1930(3)	3856(5)	2846(2)	38.8(12)
C(2)	2383(4)	4498(5)	2442(2)	42.1(14)
C(3)	2899(3)	5338(5)	2807(2)	37.2(12)
C(4)	3414(3)	6242(5)	2551(2)	45.4(13)
C(5)	5349(4)	4514(6)	3042(3)	75(2)
C(6)	5043(4)	4443(6)	4129(3)	64(2)
C(7)	5255(5)	2756(6)	3551(3)	76(2)
C(8)	4639(4)	2020(6)	3850(3)	67(2)
C(9)	3040(4)	1630(5)	3854(3)	67(2)
C(10)	3626(5)	1283(6)	2880(3)	76(2)
C(11)	2569(3)	5411(4)	3429(2)	31.6(11)
C(12)	1990(3)	4504(4)	3464(2)	30.5(11)
C(13)	1708(3)	4313(4)	4059(2)	32.2(11)
C(14)	1937(3)	5090(4)	4559(2)	37.4(12)
C(15)	2471(3)	6011(4)	4491(2)	36.6(13)
C(16)	2821(3)	6160(4)	3930(2)	33.6(12)
C(17)	1360(5)	2761(6)	4681(3)	72(2)
O(2)	1613(2)	4952(3)	5126(2)	54.0(11)
C(18)	2440(7)	4588(10)	5715(5)	49(2)
C(18′)	548(7)	5275(10)	4945(5)	49(2)
C(19)	3091(4)	7731(5)	4915(3)	54(2)
C(21)	1290(4)	2978(5)	2563(2)	50.3(15)
C(22)	1484(5)	2368(5)	2042(3)	60(2)
C(23)	842(6)	1596(5)	1718(3)	79(2)
C(24)	15(6)	1432(6)	1912(4)	98(3)
C(25)	−177(5)	2038(7)	2425(3)	87(2)
C(26)	452(4)	2800(6)	2743(3)	67(2)
C(31)	2764(4)	7124(5)	2228(2)	44.6(13)
C(32)	2627(5)	8097(5)	2539(3)	62(2)
C(33)	2013(6)	8867(6)	2241(3)	86(2)
C(34)	1505(6)	8664(6)	1612(3)	95(3)
C(35)	1637(6)	7716(6)	1302(3)	79(2)
C(36)	2243(4)	6950(5)	1598(3)	60(2)
C(99)	3841(4)	965(6)	5814(3)	64(2)
S	4601.6(15)	2107(2)	6023.4(8)	88.8(7)
O(4)	4368(5)	2580(5)	6577(3)	139(3)
O(5)	4454(4)	2749(4)	5447(2)	109(2)
O(6)	5492(3)	1516(8)	6157(3)	166(4)
F(1)	4005(4)	427(4)	5307(2)	112(2)
F(2)	2986(3)	1305(5)	5672(3)	150(2)
F(3)	3886(3)	262(4)	6299(2)	94.4(14)
C(98)	207(5)	9060(7)	3888(4)	94(2)
Cl(1)	−864(3)	9349(4)	4264(2)	80(2)
Cl(2)	877(6)	8385(11)	4477(5)	217(6)
Cl(3)	411(7)	10200(5)	3589(4)	209(5)
Cl(1′)	1357(4)	9816(5)	3770(3)	107(2)
Cl(2′)	−455(4)	10126(6)	3887(4)	145(4)
Cl(3′)	654(5)	8310(7)	4544(4)	105(3)

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

coordination (0−0.2 Å).[14,29,30] The same occurs with the *slip angles* ψ (the angles between the normal to the plane through the metal atom and the centroid−metal vector)[14,29,30c] (12.7, 12.4°), which lie between the corresponding values observed in η^3- (or η^3-C_5H_5) (20−24°) and η^5-complexes (2−5°).[29,30c] However, whereas the *fold angles* (dihedral angles between the plane defined by the three allylic carbons and that formed by the benzenoid carbons)[9] (7, 10°) are in the range corresponding to η^5-complexes (7.4−10°; the η^3-complexes show values of 20−26°),[30c] the *slip distortions*, Δ (distance between the C_5 ring centroid and the projection of the metal atom on the ring)[14,29,30c] (0.44, 0.39 Å), are near to the lowest limit of 0.3 Å proposed for an η^3-coordination.[29] In addition, C−C bond distances within the allylic and benzenoid fragments (C(1−3), C(11)/(12), respectively) are significantly shorter than the bonds between them (see figure captions), which supports an η^3-coordination. In consequence, we cannot assign unambigously the hapticity of the substituted indenyl ligands in our complexes.

As expected, the methylene protons of the benzyl substituent appear as an AB system in the ^1H NMR spectra of all complexes except for **3**, which shows a deceptively simple singlet.

Conclusions

By reaction of (*o*-styrylaryl)palladium complexes with $Tl(CF_3SO_3)$ and different alkynes, highly functionalized indenyl palladium complexes are obtained. The process requires a monoinsertion of the alkyne into the C−Pd bond and a H scrambling involving a C−H bond cleavage and a C−H bond formation. The hapticity of the indenyl ligands is intermediate between η^3- and η^5-coordination. The reactions are highly specific. The regioselectivity observed with PhC≡CH is contrary to the usually found in other processes involving the monoinsertion of an alkyne into a Pd−aryl bond.

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Supporting Information Available: For **3** and **4**, tables giving crystal data and details of the structure determination, complete atom coordinates and *U* values, bond lengths and angles, and anisotropic displacement coefficients (25 pages). Ordering information is given on any current masthead page.

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