Organometallics 1987, *6*, 2043–2053

pendent non-hydrogen atoms were found with program MULTAN and subsequent Fourier difference syntheses. Refinement of their coordinates and thermal parameters, first isotropic and then anisotropic, led to the final R values reported in Table IV. For the compound **9**α, the coordinates of the hydrogen atoms were computed and their contributions introduced in the refinement with thermal parameters equal to those of the atoms to which they were bonded. For the compound **11**, the hydrogen atoms were not introduced into the refinement because of the large R and R_ω values; in this case, the last Fourier difference synthesis did not show any residual electronic density except for peaks at 1.5 e Å^{-3} close to the Pd or I atoms.

Acknowledgment. We thank Mr. R. Hueber for recording the mass spectra, Dr. A. Dedieu for helpful discussions, the CNRS for a grant (to F.M.), and the "Commission of the European Communities" for financial support of this work (Contract No. ST 2J-0090-1-F).

Registry No. 1, 18987-59-2; *cis*-1*, 109802-26-8; *trans*-1*, 109905-22-8; 1**, 109802-30-4; **2**, 28377-73-3; **2***, 109802-27-9; **2****, 109802-31-5; **3**, 18987-72-9; *cis*-**3***, 109802-28-0; *trans*-**3***, 109905-23-9; **3****, 109802-33-7; **4a**, 109802-34-8; **4a***, 109802-44-0; **4a****, 109802-48-4; **4b**, 109802-35-9; **4c**, 109802-36-0; **5a**, 109802-37-1; **5b**, 109802-38-2; **5c**, 109802-39-3; **6a**, 109802-49-5; **6b**, 109838-68-8; **6c**, 109802-50-8; **6d**, 109802-59-7; **6e**, 109802-51-9; **6f**, 109802-56-4; **6g**, 109802-57-5; **6h**, 109838-69-9; **6i**, 109802-52-0; **6j**, 109802-58-6; **7**, 71318-04-2; **8**, 109802-54-2; **8***, 109802-55-3; **9**α, 109802-53-1; **9**β, 109802-41-7; **9**γ, 109802-60-0; **10a**, 71305-20-9; **10b**, 109802-61-1; **10c**, 109802-62-2; **10d**, 109802-63-3; **11**, 109802-43-9; **12**, 109802-64-4; **13**, 109802-66-6; **14**, 109802-45-1; **15**, 109802-46-2; **16**, 109802-68-8; **17a**, 109802-70-2; **17b**, 109838-71-3; MeC≡CPh, 673-32-5; Pd, 7440-05-3; ethyl 3-phenylpropiolate, 2216-94-6; methyl 3-phenylpropiolate, 4891-38-7; dimethyl acetylenedicarboxylate, 762-42-5; diphenylacetylene, 501-65-5; hexafluorobut-2-yne, 692-50-2.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond distances and bond angles including all atoms for **9**α and **11** (15 pages); listings of observed and calculated structure factors for **9**α and **11** (43 pages). Ordering information is given on any current masthead page.

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Stepwise Insertion of One, Two, and Three Alkyne Molecules into the Pd–C Bond of a Six-Membered Palladocycle.[1] One-Pot Synthesis of Spirocyclic Compounds

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The Pd–C bond of the compound containing a six-membered palladocyclic ring [{Pd(BP)(μ-Cl)}$_2$] (**1**) (BP = $C_6H_4CH_2C_5H_4N$-2-(2-picolyl)phenyl) reacted with one alkyne unit ($R^1C{\equiv}CR^2$ in which R^1 and/or R^2 = Me, Ph, or CO_2R and R = Me or Et) to afford regioselectively [{Pd(C(R^2)=C(R^1)$C_6H_4CH_2C_5H_4N$)(μ-Cl)}$_2$] (**2a–f**). The geometry of these eight-membered ring containing complexes was determined by an X-ray diffraction study of one of their corresponding monomers, [Pd{C(Ph)=C(CO_2Et)$C_6H_4CH_2C_5H_4N$}(2-MeC_5H_4N)Cl] (**3″a**), obtained by reaction of **2a** with 2-methylpyridine. The structure revealed that the carbon and the nitrogen atom bonded to the palladium are cis to each other. It also showed that the more electron-withdrawing group of the alkyne (R^1 = CO_2Et) is close to the benzyl ring of the BP ligand. The iodide-bridged derivative **1*** reacted with diphenylacetylene in refluxing chlorobenzene to afford a mixture of two products, **7a** and **8a**, which contain the heterocyclic cation [C(Ph)=C(Ph)$C_6H_4CH_2C_5H_4N$] with a Pd_2I_6 dianion or an iodide ion, respectively. Compounds **2c**, **2d**, and **2f** underwent insertion of a second alkyne (R^1, R^2 = Me, Ph) leading to the series of compounds **4a–g**. The X-ray diffraction of **4a** revealed the cyclization of two alkyne molecules with one carbon atom of the benzyl unit. This led to a spiro junction between a tetraphenylcyclopentadiene and a hexadienyl ring. This latter is η^3-bonded to Pd. Compound **4a** rearranged in refluxing chlorobenzene leading to a thermodynamically more stable isomer, **5a**. The reaction between the ionic compound [Pd{C(CO_2Me)=C(CO_2Me)$C_6H_4CH_2C_5H_4N$}($MeCN$)$_2$]SO_3CF_3 (**2e****) and dimethyl acetylenedicarboxylate (DMAD) afforded complex **6** in which three alkyne molecules have been found per Pd atom. The molecular structure of **6** has been determined by means of X-ray diffraction. It revealed that the two alkynes that have been added on **2e**** formed again a cyclopentadiene ring with one quaternary carbon atom. The new terdentate ligand is chelating the Pd atom via the nitrogen, carbon, and oxygen atoms, defining thus two metalated rings containing seven and five atoms, respectively.

Introduction

The metal–carbon σ-bond of cyclometalated complexes is reactive toward various nucleophilic reagents.[3] In most cases these reactions lead to the selective functionalization of the metalated chelate; thus, they might be useful for the purpose of organic syntheses. A few such reagents can, however, react with metal–carbon bonds affording stable organometallic compounds in which the resulting new ligand is still interacting with the metal.[4-7] We are mostly

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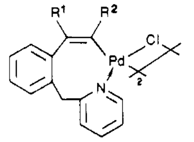
[1] Reaction of Cyclopalladated Compounds. 16. Part 15: *Organometallics*, preceding paper in this issue.

[2] (a) Laboratoire de Chimie de Coordination. (b) Laboratoire de Cristallochimie.

[3] Ryabov, A. D. *Synthesis* 1985, 233.

Table I. Analytical and Spectroscopic Data for Compounds 2a–f

	anal. found[a]				IR (KBr)	
	C	H	N	yield, %	$\nu_{C=O}$, cm^{-1}	^{1}H NMR (CDCl$_3$, δ (ppm), J (Hz))
2a: $R^1 = CO_2Et$; $R^2 = Ph$	55.19 (57.04)	3.92 (4.13)	2.09 (2.89)	82	1690 (vs, br)	8.89 (dd, 1 H, H_o), 8.63 (dd, 1 H, H_p),[d] 4.47–4.00 (m, 2 H, CH_2, $^2J_{H_A-H_B}$ = 16.5), 3.83 (qd, 2 H, OCH_2), 0.80 (m, 3 H, CH_3)
2b: $R^1 = CO_2Me$; $R^2 = Ph$	55.63 (56.18)	3.76 (3.83)	3.26 (2.98)	74	1690 (vs, br)	8.90 (dd, 1 H, H_o, $^3J_{H_o-H_m}$ = 6.0, $^4J_{H_o-H_p}$ = 1.4), 8.64 (dd, 1 H, H_p, $^3J_{H_p-H_m}$ = 5.7), 4.46–4.00 (m, 2 H, CH_2), 3.42 and 3.35 (2s, 3 H, OCH_3)
2c: $R^1 = Me$; $R^2 = Ph$		*b*		72		8.71 (d, 1 H, H_o, $^3J_{H_o-H_m}$ = 5.5), 4.44–3.93 (m, 2 H, CH_2), 1.93 and 1.91 (2s, 3 H, CH_3)
2d: $R^1 = R^2 = Ph$		*b*		86		8.94 (dd, 1 H, H_o, $^3J_{H_o-H_m}$ = 4.3), 8.71 (dd, 1 H, H_p, $^3J_{H_p-H_m}$ = 4.4), 4.62–4.03 (m, 2 H, CH_2, $^2J_{H_A-H_B}$ = 15.9)
2e: $R^1 = R^2 = CO_2Me$	47.43 (47.79)	3.31 (3.54)	3.06 (3.09)	91	1700 (vs)	8.81 (dd, 1 H, H_o), 8.60 (dd, 1 H, H_p), 4.29–4.02 (m, 2 H, CH_2, $^2J_{H_A-H_B}$ = 16.3), 3.83–3.59 (m, 6 H, OCH_3)
2f: $R^1 = R^2 = Me$		*b*		*c*		3.82 (m, 2 H, CH_2), 2.19–1.67 (m, 6 H, CH_3)

[a] Calculated values are given in parentheses. [b] Satisfactory analytical data could not be obtained (see text). [c] Not isolated. [d] H_o, H_m, and H_p represent the protons ortho, meta, and para to the nitrogen atom of the benzylpyridine ligand, respectively.

interested in these latter "insertion" reactions since we believe that they can provide important information regarding the exact role of the metal during the reactions, e.g., carbon–carbon and carbon–nitrogen bond formations. In this respect we have been so far mainly concerned with the reactions of alkynes with cyclometalated compounds.

We are aware of only a few independent studies that have been reported in the literature. For example, cyclometalated triphenylphosphine complexes of Ru and Rh,[6] containing a four-membered ring, allowed the insertion of two alkyne molecules into their M–C bonds to afford eight-membered rings. We, and others, have shown[7] that five-membered rings derived from metalated tertiary amines undergo similar reactions, and recently we have also demonstrated that even seven-membered[8] cyclopalladated rings may still be reactive toward alkynes. Therefore, we thought it of interest to extend this study to the less common six-membered cyclometalated complexes in order to determine to what extent the size of the starting organometallic ring determines the scope of the reaction. Compounds containing this type of metallocyclic unit, in which the donor atom is nitrogen,[9] phosphorus,[10] or oxygen[10a,11] have been reported in the literature.

Recently, Fuchita et al. described the synthesis of such a compound starting from 2-benzylpyridine (BP) and palladium(II) acetate;[9b] these authors have also shown that its Pd–C bond had a reactivity toward alkenes[9b] similar to that of the related five-membered ring.[12] Thus, this palladocycle is nicely suited to our purpose.

In this paper, we report that the Pd–C bond of this type of metallocycle is, as expected, reactive toward alkyne insertion and, furthermore, that this type of starting organometallic ring leads in fact to a very rich chemistry. Some aspects of this work have already been reported in a short communication.[13]

Results

1. Reactivity of Cyclopalladated Benzylpyridine Complexes Containing Chloride Bridges. 1.1. Insertion of One Alkyne into the Pd–C Bonds of 1. The poorly soluble cyclopalladated complex [{Pd(BP)(μ-Cl)}$_2$] (1) reacted in refluxing CH_2Cl_2 with ethyl 3-phenylpropiolate in a 1:2 stoichiometry (one alkyne per Pd atom) to afford a yellow solution from which compound **2a** could be isolated in quantitative yield. Elemental analyses (C, H, N) are consistent with a molecule in which one alkyne has reacted with each palladium center. The complexity of the ^{1}H NMR spectrum is an indication of the presence of several isomers.[8] The cleavage of the chloride bridges by pyridine or triphenylphosphine led to the monomeric compounds **3a** and **3′a**, respectively. The ^{1}H NMR spectrum of each of these two complexes reveals the presence of two isomers in a 97:3 ratio. We have shown previously[14] that a phosphine ligand is very unlikely to be bonded to Pd trans to a σ-bonded carbon; therefore in **3a** and **3′a**,

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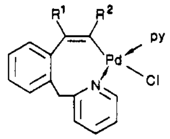
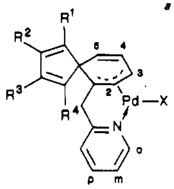
Table II. Analytical and Spectroscopic Data for Compounds 3a–f

	anal. found[a]			IR (KBr)	
	C	H	N	$\nu_{C=O}$, cm^{-1}	^1H NMR ($CDCl_3$, δ (ppm), J (Hz))
3a: $R^1 = CO_2Et$; $R^2 = Ph$	59.72 (59.69)	4.45 (4.44)	4.97 (4.97)	1680 (vs)	9.32 (dd, 1 H, H_o, BP, $^3J_{H_o-H_m} = 5.8$), 8.08 (dd, 2 H, H_o, py, $^3J_{H_o-H_m} = 6.5$, $^4J_{H_o-H_p} = 1.6$), 4.58 and 4.17 (2d, 2 H, CH_2, $^2J_{H_A-H_B} = 16.1$), 3.83 (q, 2 H, OCH_2), 0.81 (t, 3 H, CH_3)
3b: $R^1 = CO_2Me$; $R^2 = Ph$	57.37 (57.35)	4.23 (4.12)	4.96 (4.91)[b]	1705 (vs)	9.32 (dd, 1 H, H_o, BP, $^3J_{H_o-H_m} = 5.8$, $^4J_{H_o-H_p} = 1.4$), 8.07 (dd, 2 H, H_o, py, $^3J_{H_o-H_m} = 6.5$, $^4J_{H_o-H_p} = 1.6$), 4.58 and 4.18 (2d, 2 H, CH_2, $^2J_{H_A-H_B} = 16.3$), 3.39 (s, 3 H, OCH_3)
3c: $R^1 = Me$; $R^2 = Ph$	61.76 (61.79)	4.37 (4.55)	5.34 (5.54)		9.40 (dd, 1 H, H_o, BP, $^3J_{H_o-H_m} = 7.1$, $^4J_{H_o-H_p} = 1.5$), 8.11 (dd, 2 H, H_o, py, $^3J_{H_o-H_m} = 5.1$), 4.47 and 4.10 (2d, 2 H, CH_2, $^2J_{H_A-H_B} = 16.0$), 1.94 (s, 3 H, CH_3)
3d: $R^1 = R^2 = Ph$	64.97 (65.62)	4.16 (4.41)	4.78 (4.94)		9.24 (dd, 1 H, H_o, BP, $^3J_{H_o-H_m} = 5.8$, $^4J_{H_o-H_p} = 1.3$), 8.45 (dd, 2 H, H_o, py, $^3J_{H_o-H_m} = 6.4$, $^4J_{H_o-H_p} = 1.4$), 4.61 and 4.18 (2d, 2 H, CH_2, $^2J_{H_A-H_B} = 16.1$)
3e: $R^1 = R^2 = CO_2Me$	51.65 (51.98)	3.94 (3.95)	5.16 (5.27)	1700 (vs)	9.08 (dd, 1 H, H_o, BP), 8.67 (s, (br), 2 H, H, py), 8.33 (dd, 2 H, H_o, py, $^3J_{H_o-H_m} = 5.2$), 4.40 and 4.19 (2d, 2 H, CH_2, $^2J_{H_A-H_B} = 16.8$), 3.71 and 3.60 (2s, 6 H, OCH_3)
3f: $R^1 = R^2 = Me$		c			9.28 (dd, 1 H, H_o, BP, $^3J_{H_o-H_m} = 4.6$), 8.77 (dd, 2 H, H_o, py, $^3J_{H_o-H_m} = 4.9$), 8.35 (dd, 1 H, H_p, BP, $^3J_{H_p-H_m} = 5.0$), 4.25 and 3.92 (2d, 2 H, CH_2, $^2J_{H_A-H_B} = 16.0$), 1.88 and 1.74 (2s, 6 H, CH_3)

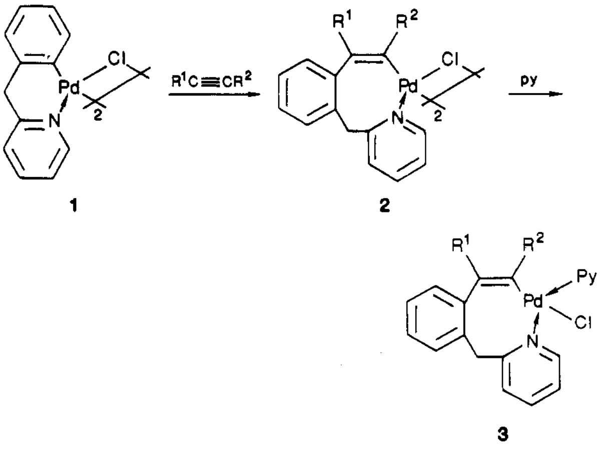
[a] Calculated values are given in parentheses. [b] The analyses have been calculated for a molecule containing 0.25 molecule of dichloromethane. [c] Not isolated.

Table III. Analytical Data, Reaction Conditions, and Yields for Compounds 4 and 5

	anal. found[b]				
	C	H	N	yield, %	refluxing time, h (solv)
4a: $R^n = Ph$	71.3	4.34	2.08	88	18 (CH_2Cl_2)
5a: $R^n = Ph$	71.88 (72.08)	4.36 (4.50)	1.37 (2.10)	50	0.33 (C_6H_5Cl)
4a*: $R^n = Ph$	63.40	3.88	1.81	70[c]	0.5 (C_6H_5Cl)
5a*: $R^n = Ph$	62.99 (63.38)	3.89 (3.96)	1.58 (1.84)		
4b: $R^1 = R^2 = R^3 = Ph$; $R^4 = Me$		d		76[c]	6 (CH_2Cl_2)
4c: $R^1 = R^2 = R^4 = Ph$; $R^3 = Me$	65.05 (65.90)	4.37 (4.48)	2.12 (2.16)[e]		
4d: $R^1 = R^4 = Me$; $R^2 = R^3 = Ph$		d		60[c]	12 (CH_2Cl_2)
4e: $R^1 = R^3 = Me$; $R^2 = R^4 = Ph$	67.91 (68.37)	5.13 (5.10)	2.41 (2.38)[e]		
4f: $R^n = Me$	57.43 (57.43)	5.34 (5.26)	3.34 (3.35)	48	20 (CH_2Cl_2)[f]
4g: $R^1 = R^2 = Ph$; $R^3 = R^4 = Me$	65.02 (64.86)	5.08 (5.02)	2.56 (2.70)	74	20 (CH_2Cl_2)[f]

[a] The spiro ligand is η^3-bonded to Pd center via C1, C2, and C3 in **4** and C3, C4, and C5 in **5**. [b] Calculated values are given in parentheses. [c] The yield refers to a mixture of the two isomers **4a***:**5a***, **4b**:**4c**, and **4d**:**4e** which are present in ca. 1:1 ratio (checked by ^1H NMR) in the crude reaction product. [d] Not isolated. [e] The analyses have been calculated for a molecule containing 0.5 molecule of dichloromethane (**4c**) and 0.5 molecules of toluene (**4e**) (the amounts of the solvents have been determined by ^1H NMR). [f] The reaction was run at room temperature.

both the pyridine and the phosphine ligands should be coordinated trans to the nitrogen of the eight-membered ring.



1 **2** **3** (1)

Thus, the two isomers found in **3a** and **3′a** resulted from a nonregiospecificity of the insertion reaction. The relative positions of the phenyl and CO_2Et substituents in the major isomer have been determined by an X-ray study of **3″a**[15a] (vide infra). It shows that the phenyl group is located on the carbon atom σ-bonded to Pd. This indicated that the orientation of the alkyne insertion ($PhC\equiv CCO_2Et$) into the Pd–C bond of **1** compares well with our previous observations for related starting materials.[8]

A view of the molecular structure and selected bond distances and angles are given in Figure 1 and Table V, respectively. This structure shows that the two nitrogen atoms of the pyridine rings are indeed trans to each other,

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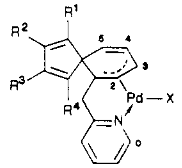
(15) (a) Crystals suitable for single-crystal X-ray analysis could only be obtained by using 2-methylpyridine as a ligand (**3″a**). (b) See selections of least-squares planes of compounds **3″a**, **4a**, and **6** which are given in the supplementary material (Tables S13–S15). (c) The dihedral angle between the planes defined by Pd, Cl1, N1, N2, C2 and C3–C8 in **3″a** is 61.8°.[15b]

Table IV. ^{1}H NMR (δ (ppm), *J* (Hz)) for the Spiro Compounds 4 and 5 in $CDCl_3$



	H5 ($^3J_{H5\text{-}H4}$)[a]	H4 ($^3J_{H4\text{-}H3}$)[b]	H3[c]	H2 ($^3J_{H2\text{-}H3}$)[a]	H6 ($^3J_{H_o\text{-}H_m}$)[b]	H$_p$ ($^3J_{H_m\text{-}H_p}$)[d]	CH$_2$ ($^2J_{H_A\text{-}H_B}$)[e]	R^n[f] R^1	R^2	R^3	R^4
4a	5.68 (9.0)	6.08 (5.5)	4.65	5.98 (6.1)	7.64 (4.2)	7.44 (7.2)	3.60 3.49 (16.8)				
4a*	5.76 (8.4)	6.11 (5.7)	4.78	5.99 (5.9)	7.88 (4.2)	7.41 (7.7)	3.70 3.60 (16.5)				
5a	5.35 (9.0)	6.09 (5.4)	4.86	5.81 (5.8)	8.66 (4.7)	7.77 (7.4)	3.26 3.06 (16.0)				
5a*	5.40 (9.3)	6.11 (5.2)	4.98	5.82 (5.9)	8.90 (4.1)	7.72 (7.4)	3.40 3.13 (15.9)				
4b	5.39 (9.0)	6.57 (5.7)	4.86	5.71 (ca. 5.5)	8.78 (4.2)	7.85 (7.5)	3.19 (n.o.)[g]				1.79
4c	5.74 (8.7)	6.25 (5.3)	4.75	5.71 (5.5)	7.65 (5.2)	7.53 (7.7)	3.17 3.09 (16.8)			1.92	
4d	5.09 (9.2)	6.14 (5.4)	5.05	6.27 (5.9)	8.75 (5.4)	7.76 (7.8)	3.35 3.06 (16.3)	1.69			1.76
4e	5.39 (9.1)	6.18 (5.6)	4.97	6.24 (5.9)	7.67 (5.2)	n.o.	3.14 2.98 (16.7)	1.67		1.85	
4f	4.78 (9.2)	5.99 (5.7)	4.96	6.16 (6.0)	8.69 (5.4)	6.77 (7.7)	3.15 2.72 (16.2)	1.55	1.61	1.81	1.52
4g	5.27 (9.1)	6.17 (5.5)	4.83	5.70 (5.8)	8.72 (4.3)	7.73 (7.7)	3.12 3.03 (15.9)			1.75	1.64

[a] Doublet (d). [b] Doublet of doublet (dd). [c] Triplet (t). [d] Doublet of triplet (td). [e] Two doublets (2d). [f] Only the chemical shifts of R^n = Me are given. [g] n.o. = not observed.

Table V. Selected Bond Distances (Å) and Angles (deg) for Compound 3″a

Bond Distances			
Pd-C1	2.005 (3)	C9-C10	1.513 (5)
C1-C2	1.320 (5)	C10-N1	1.337 (4)
C2-C3	1.501 (5)	N1-Pd	2.084 (3)
C3-C8	1.384 (5)	N2-Pd	2.052 (3)
C8-C9	1.508 (6)	Cl1-Pd	2.424 (1)
Bond Angles			
Cl1-Pd-C1	174.13 (9)	C10-C9-C8	119.4 (3)
N1-Pd-N2	171.8 (1)	C9-C8-C3	120.6 (3)
Cl1-Pd-N2	89.11 (8)	C8-C3-C2	118.5 (3)
N2-Pd-C1	85.6 (1)	C3-C2-C1	119.9 (3)
C1-Pd-N1	93.5 (1)	C2-C1-Pd	119.6 (2)
Pd-N1-C10	130.5 (2)		
N1-C10-C9	122.0 (3)		

whereas the chlorine atom is trans to the carbon C1 of the new alkenyl moiety σ-bonded to Pd.

Several least-squares planes of the molecule are given in Table S13. They allow a comparison of the geometry of the new organometallic eight-membered ring with those of related seven-membered rings.[7a,b] The main effect of the presence of one extra atom in the metallocycle is to decrease the dihedral angle between the plane of the phenyl ring (C3–C8) and that of the coordination plane of Pd[15b] to a value close to 60°. This dihedral angle was close to 90° in a related seven-membered metallocycle.[7a,b] Thus, it appears that in this new metalated ring one apical coordination site of the Pd is much more hindered than in the previous cases.

Treating compound 1 with a series of alkynes (1-phenylprop-1-yne, diphenylacetylene, methyl 3-phenylpropiolate) affords compounds **2b–e**, whose formulas are closely related to that of **2a**; i.e. one alkyne molecule has been inserted into the Pd–C bond of 1 leading to eight-membered rings. It has to be noted, however, that in the cases of the reactions of 1 with 1-phenylprop-1-yne and diphenylacetylene, which afforded **2c** and **2d**, respectively, the syntheses were difficult because these mono-inserted products reacted further with unreacted alkyne, even when a strict 1:2 stoichiometry was used. Moreover, despite all our efforts to crystallize the products no satisfactory analytical data could be obtained.[16] However, the formulations of **2c** and **2d** were ascertained by the syntheses of the monomers **3c** and **3d**, whose analytical data are satisfactory (see Table II). These two monomeric species were obtained either by treating **2c** and **2d** with pyridine or more easily from the reaction between the monomer [Pd(BP)pyCl][17] and the corresponding alkynes.

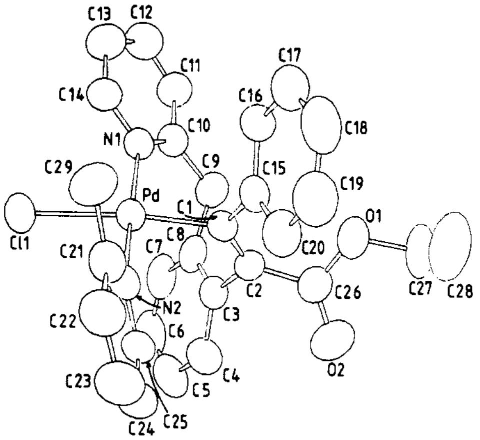


Figure 1. ORTEP view of [Pd{C(Ph)=C(CO$_2$Et)C$_6$H$_4$CH$_2$C$_5$H$_4$N}(2-MeC$_5$H$_4$N)Cl] (3″a).

1.2. Further Alkyne Insertion into the New Pd–C Bond of 2. We have already mentioned that in the case of the reactions between 1 and alkynes substituted by Ph and Me groups (e.g., diphenylacetylene, 1-phenylprop-1-yne, and 2-butyne) it was difficult to stop the reaction at the stage of mono-inserted products **2c**, **2d**, or **2f**. Indeed,

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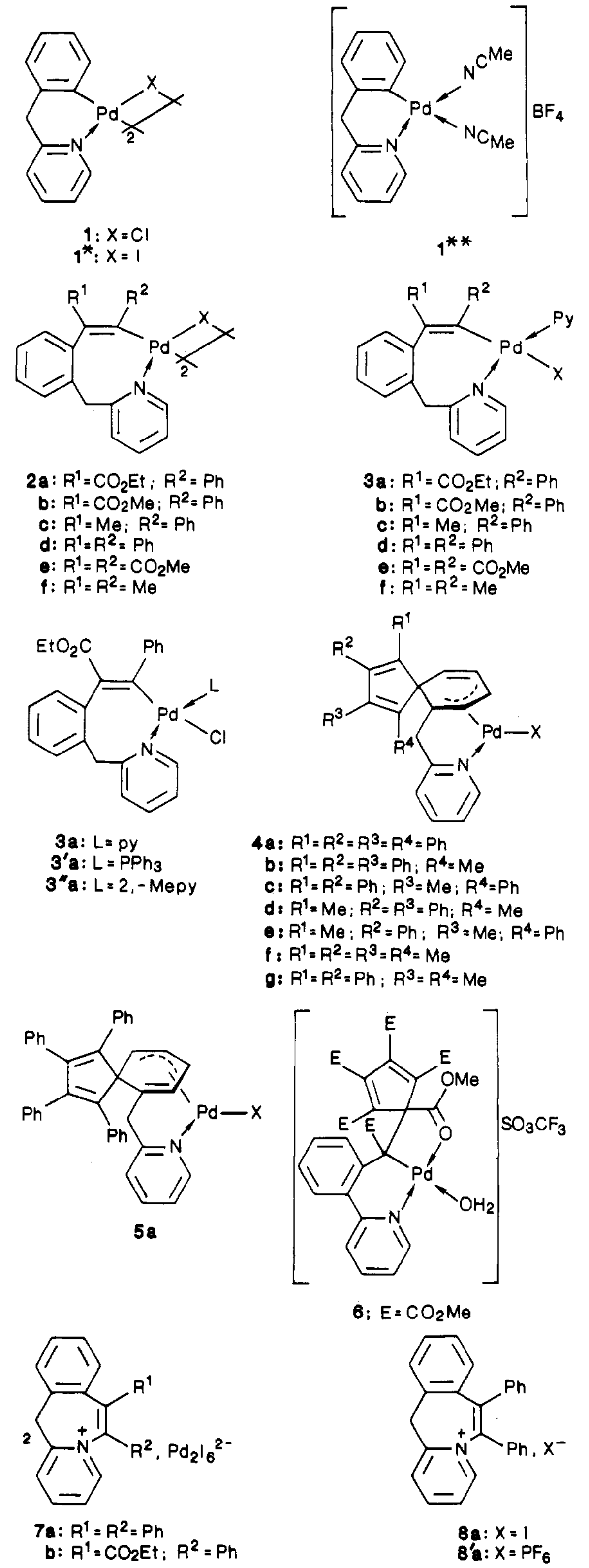
[16] Anal. Calcd for $C_{28}H_{20}ClNPd$ (**2d**): C, 63.94; H, 4.09; N, 2.86. Found: C, 53.30; H, 3.52; N, 2.89. We cannot give a rational explanation for the values found for the percentage of carbon present. A similar trend for this analysis has however be observed in other organopalladium compounds: Dehand, J.; Pfeffer, M.; Zinsius, M. *Inorg. Chim. Acta* **1975**, *13*, 229.

[17] This product was obtained by reaction of 1 with 1 equiv of pyridine.[9b]

Chart I[a]



1: X = Cl
1*: X = I

1**

2a: $R^1 = CO_2Et$; $R^2 = Ph$
b: $R^1 = CO_2Me$; $R^2 = Ph$
c: $R^1 = Me$; $R^2 = Ph$
d: $R^1 = R^2 = Ph$
e: $R^1 = R^2 = CO_2Me$
f: $R^1 = R^2 = Me$

3a: $R^1 = CO_2Et$; $R^2 = Ph$
b: $R^1 = CO_2Me$; $R^2 = Ph$
c: $R^1 = Me$; $R^2 = Ph$
d: $R^1 = R^2 = Ph$
e: $R^1 = R^2 = CO_2Me$
f: $R^1 = R^2 = Me$

3a: L = py
3′a: L = PPh_3
3″a: L = 2,-Mepy

4a: $R^1 = R^2 = R^3 = R^4 = Ph$
b: $R^1 = R^2 = R^3 = Ph$; $R^4 = Me$
c: $R^1 = R^2 = Ph$; $R^3 = Me$; $R^4 = Ph$
d: $R^1 = Me$; $R^2 = R^3 = Ph$; $R^4 = Me$
e: $R^1 = Me$; $R^2 = Ph$; $R^3 = Me$; $R^4 = Ph$
f: $R^1 = R^2 = R^3 = R^4 = Me$
g: $R^1 = R^2 = Ph$; $R^3 = R^4 = Me$

5a

6; E = CO_2Me

7a: $R^1 = R^2 = Ph$
b: $R^1 = CO_2Et$; $R^2 = Ph$

8a: X = I
8′a: X = PF_6

[a] Throughout this paper we have used the nomenclature of *n* (**1**–**5**) for the complexes in which X = Cl, *n** for the complexes in which X = I, and *n*** for the corresponding cationic complexes.

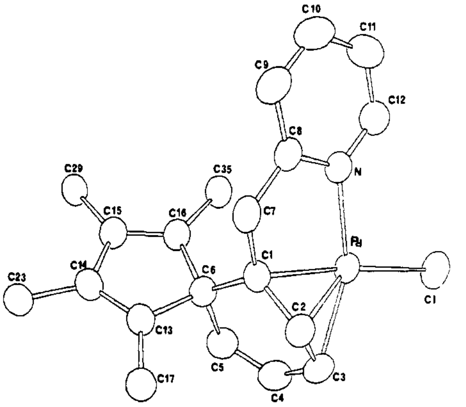


Figure 2. ORTEP view of $[\overline{Pd\{(\eta^3\text{-}C_6H_4C(Ph)=C(Ph)C(Ph)}\text{-}\overline{=C}(Ph))CH_2C_5H_4N\}Cl]$ (**4a**). The phenyl groups of the cyclopentadiene unit are only represented by their ipso carbon atoms for clarity.

Table VI. Selected Bond Distances (Å) and Angles (deg) for Compound 4a

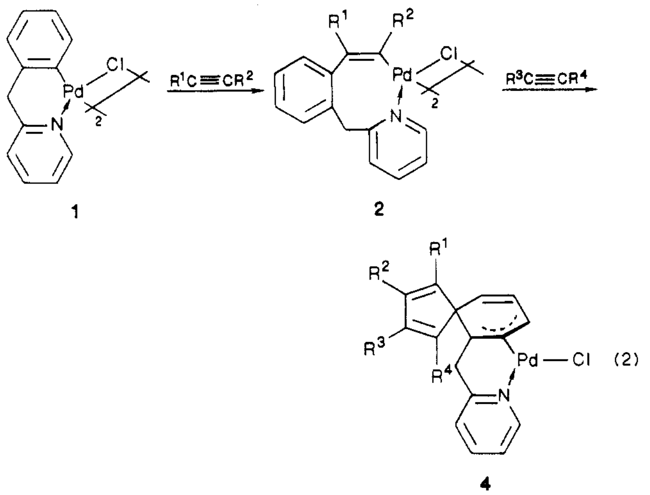
	Bond Distances		
Pd–C1	2.100 (2)	C6–C13	1.539 (3)
Pd–C2	2.047 (2)	C6–C1	1.523 (3)
Pd–C3	2.146 (2)	C1–C2	1.420 (3)
Pd–Cl	2.375 (1)	C2–C3	1.409 (3)
Pd–N	2.137 (2)	C3–C4	1.453 (4)
C1–C7	1.513 (3)	C4–C5	1.326 (3)
C7–C8	1.500 (3)	C5–C6	1.519 (3)
C6–C16	1.511 (3)		
	Bond Angles		
Cl–Pd–N	104.59 (5)	C1–C6–C5	112.5 (2)
N–Pd–C1	82.02 (7)	C13–C6–C16	102.2 (2)
N–Pd–C3	148.81 (9)	C2–C1–C7	121.4 (2)
C1–Pd–C2	40.03 (8)	C1–C7–C8	114.1 (2)
C2–Pd–C3	39.2 (1)	C1–C2–C3	114.8 (2)
C1–Pd–C3	68.32 (9)		
C1–Pd–Cl	172.06 (6)		

treating **1** with excess of diphenylacetylene in refluxing CH_2Cl_2 affords quantitatively compound **4a**, which has been shown by analytical data to contain two alkyne units per palladium atom. The ^1H NMR spectrum of **4a** reveals that four aromatic protons of the 2-benzylpyridine ligand have been dramatically shifted to higher field (see Table IV). The same phenomenon was observed for the corresponding carbon atoms in the ^{13}C NMR spectrum. These observations suggest a significant change of the bonding mode of the 2-benzylpyridine ligand to the Pd atom. In order to determine unambiguously the molecular structure of this new molecule, an X-ray diffraction study was carried out on **4a**. An ORTEP view of this complex is shown in Figure 2. Selected angles and distances and least-squares planes are given in Tables VI and S14, respectively. The addition of the second alkyne molecule into the Pd–C bond of **2d** has resulted in a totally unexpected rearrangement of the organometallic product compared to that which would be predicted according to previous related work.[8]

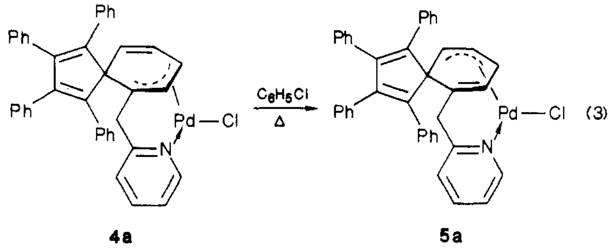
The molecular structure shows indeed the formation of a spiro junction between a tetraphenylcyclopentadiene and an hexadienyl unit. The palladium atom is linked to this new organic fragment via the nitrogen atom and an η^3-allylic interaction of the benzyl ring through C1–C3. This latter bonding mode explains the high-field shifts observed in the NMR spectra and results from the dearomatization of the phenyl ring of the BP ligand.

A compound similar to **4a** was obtained in good yield by treating **1** with an excess of 2-butyne to afford **4f**. The ^1H NMR spectrum is closely related to that of **4a**. This compound proved, however, to be much less stable in solution as it decomposed at room temperature in CH_2Cl_2 solution after several hours.

That **2d** and **2f** are intermediates in the formation of **4a** and **4f**, respectively, was easily demonstrated by reacting them with diphenylacetylene and 2-butyne, respectively. Other compounds of the same series were obtained by the reaction of **2c** or **2d** with alkynes substituted by methyl and/or phenyl groups. This led to compounds in which the cyclopentadiene units have various combinations of methyl and phenyl substituents (see Tables III and IV).



We have found that **4a** is not stable at high temperature; it isomerized in refluxing chlorobenzene to afford compound **5a**, whose NMR spectra (^{1}H, ^{13}C) are slightly different to those of **4a**. We suggest that in **5a** the C1–C6 ring is η^3-bonded to Pd via the C3, C4, and C5 atoms. The driving force for this reaction could be assigned to the release of some steric hindrance that the 2-picolyl group exerts in **4a**, which does not exist in **5a**.



This result could not be generalized to the other compounds of this series (**4b–f**) because they are not stable at high temperature. In refluxing chlorobenzene, they were decomposed to give metallic palladium together with other undetermined materials.

It is noteworthy that the double-alkyne insertion into the Pd–C bond of **1** to afford spiran ligands was limited to alkynes substituted by methyl or phenyl groups. We could not synthesize any compounds of type **4** in which the cyclopentadiene ring of the spiran unit is substituted by at least one CO_2R group. Two independent methods have been attempted by reacting (i) compounds **2c** and **2d** with ethyl 3-phenylpropiolate or (ii) compounds **2a**, **2b**, and **2c** with diphenylacetylene or 1-phenylprop-1-yne. No insertion of alkyne took place in either case, the starting organometallic compounds being totally recovered even after several hours in refluxing chlorobenzene.

2. Reactivity of Cationic Complexes of Cyclopalladated Benzylpyridine. In order to overcome our inability to obtain spiran functionalized by a CO_2R group, described in the previous section, we decided to investigate the chemistry of the cationic cyclopalladated benzylpyridine complexes. We have shown previously[8] that these compounds, in which the palladium is made more electrophilic, displayed an increased reactivity of their Pd–C bonds. Moreover, the reactions carried out with such species led often to selective syntheses of heterocyclic compounds.[8]

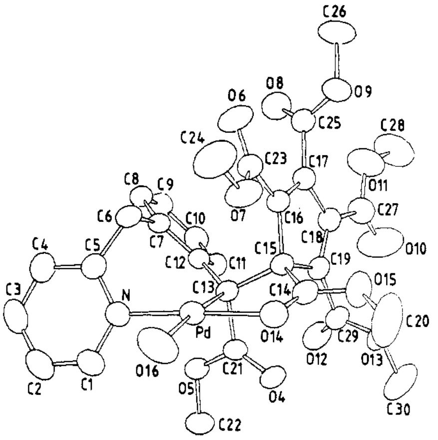


Figure 3. ORTEP view of compound **6**. The SO_3CF_3 anion has a normal geometry and is not represented.

Table VII. Selected Bond Distances (Å) and Angles (deg) for Compound 6

	Bond Distances		
Pd–O16	2.124 (2)	C13–C15	1.572 (3)
Pd–O14	2.063 (1)	C15–C14	1.530 (3)
Pd–N	2.010 (2)	C14–O14	1.229 (3)
Pd–C13	2.040 (2)	C15–C16	1.532 (3)
N–C5	1.354 (3)	C15–C19	1.525 (3)
C5–C6	1.503 (3)	C15–C13	1.572 (3)
C6–C7	1.510 (3)	C16–C17	1.337 (3)
C7–C12	1.397 (3)	C18–C19	1.341 (3)
C12–C13	1.521 (2)		
	Bond Angles		
O16–Pd–C13	174.65 (8)	Pd–C13–C15	105.7 (1)
O14–Pd–N	177.72 (6)	C13–C15–C14	107.7 (2)
Pd–N–C5	121.0 (1)	C15–C14–O14	121.0 (2)
N–C5–C6	116.1 (2)	C14–O14–Pd	113.3 (1)
C5–C6–C7	108.3 (2)	C13–C15–C16	111.9 (2)
C6–C7–C12	124.0 (2)	C16–C15–C19	100.9 (2)
C7–C12–C13	125.2 (2)	C21–C13–C15	109.0 (2)
C12–C13–Pd	122.2 (1)		

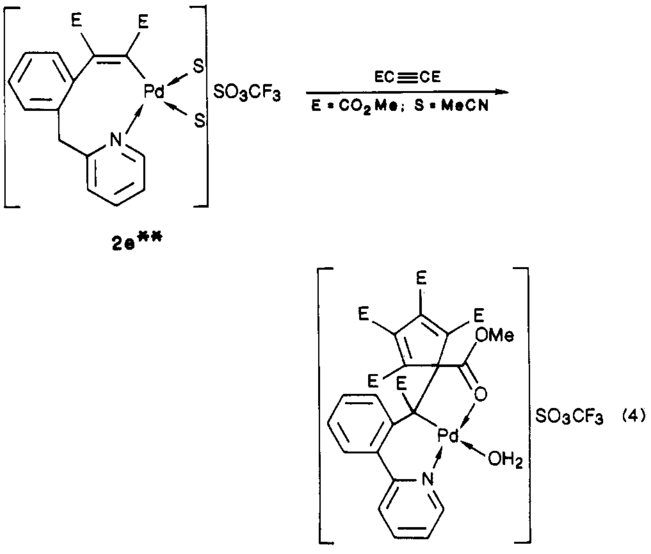
This improved reactivity of the Pd–C bond has actually been observed in the reaction between **2e**** and dimethyl acetylenedicarboxylate (DMAD). It afforded a quantitative yield of the new compound **6**. Unexpectedly, analytical data indicated that the formula of this molecule derived from that of **2e**** by addition of two DMAD units. Indeed, the ^{1}H NMR spectrum of this ionic molecule revealed the presence of six inequivalent methyl carboxylate groups. Since this is the first example of three alkynes reacting with such a palladocyclic complex, an X-ray diffraction study of **6** proved to be essential in determining its molecular geometry.

Figure 3 shows an ORTEP view of the cationic part of this molecule. It consists of a new terdentate ligand which is linked to Pd via the nitrogen atom of the benzylpyridine unit, the carbon C13, and the oxygen O14 of one carboxylate group. The fourth coordination site is occupied by a water molecule. This defines two metallocycles containing seven and five atoms, respectively. The carbon atom C15 that was σ-bonded to Pd in **2e**** has now become a spiro junction between a cyclopentadiene ring, formed with the two incoming DMAD molecules, and the five-membered metallocycle Pd–C11–C15–C14–O14. Therefore, this structure is somewhat related to that found for compound **4a**. Interestingly, the bond distance C13–C15 (1.572 (3) Å) is typical for a C–C single bond, whereas C16–C17 (1.337 (3) Å) and C18–C19 (1.341 (3) Å) have values usually assigned to C–C double bonds (Table VII).

Table VIII. Summary of Crystal Data and Intensity Data Collection of 3″a, 4a and 6

	3″a	4a	6
formula	$C_{33}H_{32}Cl_2N_2O_2Pd$ [3″a + 0.5(CH_2Cl_2 + $C_6H_5CH_3$)]	$C_{40}H_{30}ClNPd$	$C_{31}H_{30}F_3NO_{16}PdS$
cryst system	monoclinic	triclinic	triclinic
space group	*C*2/*c*	*P*1 (No. 2)	*P*1
a/Å	29.549 (7)	11.222 (8)	12.429 (13)
b/Å	9.128 (2)	16.066 (5)	12.876 (6)
c/Å	24.344 (5)	9.204 (2)	11.644 (7)
α/deg	90	98.44 (2)	104.23 (3)
β/deg	110.75 (1)	94.27 (4)	96.81 (4)
γ/deg	90	71.41 (5)	89.43 (4)
U/Å^3	6139.9	1555.1	1793.2
M_r	666	667	868
Z	8	2	2
crystal dimens/mm	0.45 × 0.35 × 0.18	0.36 × 0.29 × 0.20	0.54 × 0.45 × 0.13
λ(Mo Kα)/Å	0.71073	0.71073	0.71073
μ/cm^{-1}	8.02	7.03	6.50
F(000)	2720	680	880
scan range/deg	1.00 + 0.35 tan θ	1.00 + 0.35 tan θ	1.00 + 0.35 tan θ
θ limits/deg	1–25	1–27	1–25
reflctns, total	5908	7195	6632
reflctns, used ($I > 3\sigma(I)$)	3888	5188	5308
R factor, %	4.2	3.14	2.9
R_ω factor, %	5.6	4.29	4.1
std error in an observn of unit wt, e	1.84	1.43	1.70

A likely mechanism for the formation of this new terdentate ligand is discussed in eq 4.



The geometry of the seven-membered ring is similar to that previously observed for related metallocyclic units[7a,b,e] as can be seen from the dihedral angle between the planes defined by C6, C5, N, Pd and C6, C7, C12, C13 and the coordination plane of the Pd atom.[18] The five-membered palladocycle containing the oxygen atom in the other hand is puckered, the atom C15 being significantly out of the best least-squares plane defined by Pd, C13, C14, O14.[15b]

3. Syntheses of Heterocyclic Compounds. We have described in the preceding paper[8] that the use of cationic cyclopalladated complexes can lead to the syntheses of heterocycles by reaction with alkynes. Unfortunately, this method proved to be of no use in the case of the present study.

Table IX. Positional Parameters and Their Estimated Standard Deviations for Compound 3″a[a]

atom	*x*	*y*	*z*	*B*, Å^2
Pd	0.12035 (1)	0.12501 (4)	0.69821 (1)	3.380 (6)
Cl1	0.12797 (4)	−0.0068 (1)	0.78751 (5)	4.69 (2)
N1	0.1241 (1)	0.3273 (4)	0.7393 (2)	3.83 (8)
N2	0.1269 (1)	−0.0700 (4)	0.6598 (2)	3.78 (7)
C1	0.1114 (1)	0.2149 (4)	0.6199 (2)	3.43 (9)
O1	0.0826 (2)	0.3930 (5)	0.5145 (2)	7.3 (1)
O2	0.0257 (2)	0.2285 (7)	0.4799 (2)	10.2 (2)
C2	0.0674 (2)	0.2436 (5)	0.5830 (2)	3.89 (9)
C3	0.0249 (2)	0.2282 (5)	0.6027 (2)	4.1 (1)
C4	−0.0110 (2)	0.1219 (6)	0.5776 (3)	5.6 (1)
C5	−0.0483 (2)	0.1048 (7)	0.5998 (3)	7.2 (2)
C6	−0.0503 (2)	0.1977 (8)	0.6447 (3)	7.5 (2)
C7	−0.0163 (2)	0.3057 (7)	0.6667 (2)	6.2 (1)
C8	0.0216 (2)	0.3219 (6)	0.6459 (2)	4.6 (1)
C9	0.0545 (2)	0.4533 (5)	0.6645 (2)	5.0 (1)
C10	0.0973 (2)	0.4481 (5)	0.7216 (2)	4.1 (1)
C11	0.1094 (2)	0.5782 (6)	0.7531 (2)	5.3 (1)
C12	0.1490 (2)	0.5861 (6)	0.8028 (3)	6.1 (1)
C13	0.1763 (2)	0.4588 (7)	0.8228 (3)	6.1 (1)
C14	0.1624 (2)	0.3340 (6)	0.7898 (2)	4.7 (1)
C15	0.1557 (2)	0.2213 (5)	0.6052 (2)	3.88 (9)
C16	0.1934 (2)	0.3173 (6)	0.6361 (2)	4.7 (1)
C17	0.2359 (2)	0.3203 (7)	0.6223 (2)	6.1 (1)
C18	0.2402 (2)	0.2323 (8)	0.5789 (3)	6.9 (1)
C19	0.2043 (2)	0.1361 (8)	0.5504 (3)	6.8 (1)
C20	0.1613 (2)	0.1294 (6)	0.5625 (2)	5.5 (1)
C21	0.1699 (2)	−0.1328 (5)	0.6728 (2)	4.6 (1)
C22	0.1746 (2)	−0.2660 (6)	0.6456 (2)	5.8 (1)
C23	0.1350 (2)	−0.3252 (7)	0.6042 (3)	6.3 (1)
C24	0.0904 (2)	−0.2591 (6)	0.5913 (2)	5.6 (1)
C25	0.0881 (2)	−0.1315 (5)	0.6197 (2)	4.6 (1)
C26	0.0557 (2)	0.2896 (7)	0.5215 (2)	5.4 (1)
C27	0.0741 (3)	0.4490 (9)	0.4551 (2)	8.5 (2)
C28	0.1122 (4)	0.390 (1)	0.4345 (3)	12.2 (3)
C29	0.2132 (2)	−0.0598 (7)	0.7160 (3)	6.1 (1)
C30	0.000 (1)	−0.1008 (9)	0.750 (1)	6.0 (2)
Cl2	−0.01403 (8)	−0.2100 (2)	0.68715 (9)	9.66 (6)
C31	0.2524 (4)	−0.164 (1)	0.4628 (5)	12.4 (3)*
C32	0.2018 (6)	−0.150 (2)	0.4340 (8)	10.5 (5)*
C33	0.1754 (5)	−0.236 (2)	0.4625 (6)	17.8 (4)*
C34	0.2127 (8)	−0.319 (3)	0.516 (1)	12.7 (6)*
C35	0.2772 (5)	−0.264 (2)	0.5162 (6)	8.8 (4)*

[a] Parameters with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Two independent methods have been investigated: the thermal decomposition of **2d**** in refluxing chlorobenzene, or the reaction of **1**** with diphenylacetylene under the same conditions. Both routes led to quantitative formation of Pd^0. The spectroscopic data of the resulting organic product showed evidence for the presence of some organic

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[18] The dihedral angle in compound 6 between the planes defined by P1 (Pd, N, C5, C6) and P2 (C6, C7, C12, C13) is 101.2°. The dihedral angles between P1 and P3 (Pd, N, C13, O14, O16) and between P2 and P3 are 58.9 and 136.6°, respectively.[15b]

Table X. Positional Parameters and Their Estimated Standard Deviations for Compound 4a[a]

atom	*x*	*y*	*z*	*B*, Å^2
Pd	0.58769 (2)	0.09145 (1)	0.52522 (2)	3.099 (4)
Cl	0.68525 (7)	0.04718 (5)	0.29393 (7)	4.35 (1)
N	0.7004 (2)	−0.0024 (1)	0.6621 (2)	2.96 (4)
C1	0.4954 (2)	0.1486 (2)	0.7229 (3)	2.89 (5)
C2	0.4093 (2)	0.1459 (2)	0.6025 (3)	3.50 (5)
C3	0.4163 (3)	0.1953 (2)	0.4906 (3)	4.01 (6)
C4	0.4510 (3)	0.2757 (2)	0.5285 (3)	3.98 (6)
C5	0.4917 (2)	0.2982 (2)	0.6629 (3)	3.58 (5)
C6	0.5111 (2)	0.2383 (2)	0.7817 (3)	2.97 (5)
C7	0.5294 (2)	0.0793 (2)	0.8268 (3)	3.26 (5)
C8	0.6522 (2)	0.0079 (2)	0.7959 (3)	3.01 (5)
C9	0.7141 (3)	−0.0480 (2)	0.8990 (3)	3.99 (6)
C10	0.8223 (3)	−0.1150 (2)	0.8622 (3)	4.53 (6)
C11	0.8705 (3)	−0.1257 (3)	0.7241 (4)	4.36 (6)
C12	0.8070 (2)	−0.0675 (2)	0.6286 (3)	3.61 (5)
C13	0.4097 (2)	0.2886 (2)	0.8944 (3)	3.10 (5)
C14	0.4657 (2)	0.3161 (2)	1.0193 (3)	3.11 (5)
C15	0.6036 (2)	0.2836 (2)	1.0029 (3)	3.08 (5)
C16	0.6312 (2)	0.2351 (2)	0.8698 (3)	2.97 (5)
C17	0.2741 (2)	0.3114 (2)	0.8545 (3)	3.32 (5)
C18	0.2109 (3)	0.2500 (2)	0.8429 (3)	3.91 (6)
C19	0.0835 (3)	0.2729 (2)	0.8047 (4)	4.92 (7)
C20	0.0200 (3)	0.3553 (3)	0.7762 (5)	6.02 (9)
C21	0.0818 (4)	0.4171 (2)	0.7852 (6)	7.7 (1)
C22	0.2066 (3)	0.3959 (2)	0.8254 (5)	5.82 (8)
C23	0.3968 (2)	0.3718 (2)	1.1479 (3)	3.47 (5)
C24	0.2961 (3)	0.3530 (2)	1.1995 (3)	3.98 (6)
C25	0.2285 (3)	0.4061 (2)	1.3159 (3)	4.92 (7)
C26	0.2604 (3)	0.4775 (2)	1.3857 (4)	5.67 (8)
C27	0.3600 (4)	0.4959 (2)	1.3391 (4)	5.93 (9)
C28	0.4281 (3)	0.4445 (2)	1.2195 (4)	4.81 (7)
C29	0.6979 (2)	0.3035 (2)	1.1114 (3)	3.09 (5)
C30	0.7045 (3)	0.2863 (2)	1.2559 (3)	3.80 (6)
C31	0.7949 (3)	0.3058 (2)	1.3524 (3)	4.52 (7)
C32	0.8801 (3)	0.3409 (2)	1.3071 (4)	4.63 (6)
C33	0.8750 (3)	0.3576 (2)	1.1655 (4)	4.81 (7)
C34	0.7832 (3)	0.3400 (2)	1.0682 (3)	4.11 (6)
C35	0.7553 (2)	0.1827 (2)	0.8115 (3)	3.04 (5)
C36	0.8462 (2)	0.1290 (2)	0.8987 (3)	3.45 (5)
C37	0.9586 (2)	0.0751 (2)	0.8411 (3)	3.94 (6)
C38	0.9842 (3)	0.0720 (2)	0.6949 (4)	4.21 (6)
C39	0.8962 (3)	0.1253 (2)	0.6085 (3)	4.13 (6)
C40	0.7833 (2)	0.1802 (2)	0.6658 (3)	3.57 (5)

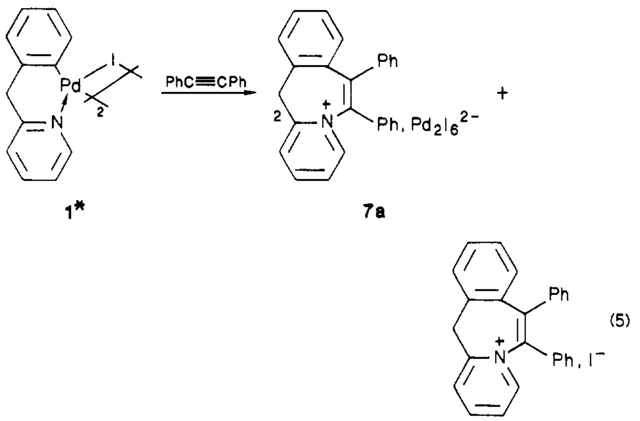
[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

cation. However, the purification of this material could not be achieved.

Another alternative method that we have discovered to promote the formation of C–N bonds from the reaction of cyclopalladated compound and alkynes was to use such complexes that contained iodide.[8]

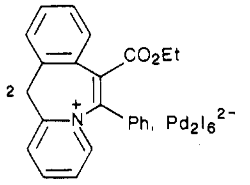
When compound **1*** was allowed to react with 2 equiv of diphenylacetylene in refluxing chlorobenzene, no organometallic compound such as **2d*** could be detected. Instead, we obtained a mixture of two products, **7a** and **8a**. Analytical and spectroscopic data indicated that these two compounds contain the same cationic organic moiety, associated with the Pd_2I_6 dianion in **7a** and an iodide in **8a**.[19]

According to previous results[8] in the related reactions of such compounds, we suggest that the cationic part in these molecules consists of a heterocyclic compound having a seven-membered ring. This should have been formed by the insertion of one alkyne into the Pd–C bond of **1*** followed by the depalladation reaction of the resulting eight-membered metallocycle **2d*** leading to a C–N bond formation via a reductive elimination process.[8]



1* **7a** **8a**

Similar behavior was observed in the case of the unsymmetrical alkyne ethyl 3-phenylpropiolate. On this occasion, the reaction was carried out starting with **2a*** (obtained from **2a** by the chloride for iodide metathesis). Nevertheless, only the heterocyclic cation associated with Pd_2I_6 dianion, **7b**, was obtained in low yield.



7b

If the reaction of **1*** with C_2Ph_2 is carried out in a 1:4 stoichiometry only trace amounts of the heterocyclic compound **7a** has been obtained; we observed an almost quantitative formation of a mixture of the compounds **4a*** and **5a***,[20] containing the spiro ligand as described above.

Discussion

This study is a supplementary illustration that the reactivity of cyclometalated complexes is not directly related to the steric strain existing in the metallocycle. Indeed, the M–C bond of six- or eight-membered rings might well be reactive toward alkyne insertion. However, when the chemistry of the complexes studied in this manuscript are compared with that of the corresponding compounds having one less atom in their metallocycle,[8] it appeared that the nature of the products formed are dramatically dependent of the size of the ring.

The ring expansion by insertion of one single alkyne into the Pd–C bond of **1** led to stable eight-membered rings in which the carbon atom σ-bonded to Pd and the coordinated nitrogen atom are still cis to each other. The insertion of an unsymmetrical alkyne occurred with high regioselectivity. Moreover, the orientation of the reaction is similar to that observed previously[8] since the more electron-withdrawing substituent of the alkyne (CO_2R vs. Ph) is found on the carbon closest to the benzyl unit. Interestingly, it has been possible, on this occasion, to isolate the products resulting from the mono-insertion of diphenylacetylene and 1-phenylprop-1-yne, this being impossible to achieve for the cyclometalated complexes studied previously.[6a,b,7a]

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[19] Treating **8a** with hot H_2O and then addition of solid NH_4PF_6 to the resulting solution afford low yields of compound **8′a** containing the PF_6 anion: IR (KBr) ν_{PF} 835 (vs) cm^{-1}, ^1H NMR ($CDCl_3$) 4.66 and 4.49 ppm (2d, 2 H, CH_2, $^2J_{H_A-H_B}$ = 13.9 Hz).

[20] We obtained a mixture of the two spiro isomers **4a*** and **5a*** (see Tables III and IV) because this reaction was performed in refluxing chlorobenzene.

Table XI. Positional Parameters and Their Estimated Standard Deviations for Compound 6[a]

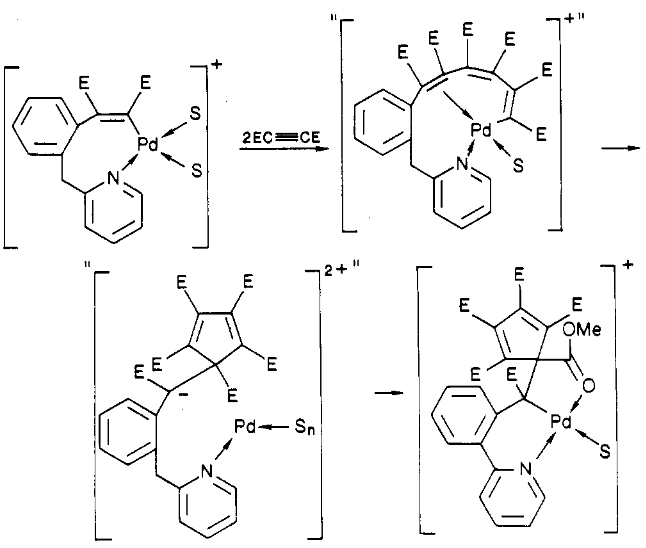
atom	*x*	*y*	*z*	*B*, Å^2
Pd	0.35290 (1)	0.30450 (1)	0.14435 (2)	2.631 (4)
O14	0.3358 (2)	0.4287 (1)	0.0610 (2)	3.19 (4)
O16	0.4088 (2)	0.4076 (2)	0.3129 (2)	5.10 (5)
N	0.3744 (2)	0.1813 (2)	0.2218 (2)	2.92 (4)
S	0.29466 (6)	0.62505 (7)	0.54590 (8)	4.69 (2)
O1	0.2987 (2)	0.5700 (2)	0.4246 (3)	6.94 (7)
O2	0.2810 (2)	0.7375 (2)	0.5599 (3)	6.97 (8)
O3	0.3745 (2)	0.5948 (3)	0.6305 (3)	7.76 (8)
O4	0.4698 (1)	0.2774 (1)	−0.0835 (2)	3.42 (4)
O5	0.4780 (1)	0.1235 (1)	−0.0252 (2)	3.06 (4)
O6	−0.0219 (2)	0.2877 (2)	0.0284 (2)	4.64 (5)
O7	0.1215 (2)	0.3952 (2)	0.1054 (2)	4.22 (4)
O8	−0.0785 (2)	0.1205 (2)	−0.2337 (2)	4.59 (5)
O9	−0.1093 (2)	0.2944 (2)	−0.2232 (2)	4.50 (5)
O10	0.1801 (2)	0.1721 (3)	−0.4842 (2)	8.64 (9)
O11	0.0139 (2)	0.1656 (3)	−0.4425 (2)	6.33 (7)
O12	0.3909 (2)	0.1539 (2)	−0.3239 (2)	4.51 (5)
O13	0.3690 (2)	0.3265 (2)	−0.3209 (2)	4.31 (4)
O15	0.2755 (2)	0.4646 (1)	−0.1124 (2)	4.21 (5)
C1	0.4733 (2)	0.1643 (2)	0.2735 (3)	3.58 (6)
C2	0.4907 (3)	0.0885 (3)	0.3373 (3)	4.41 (7)
C3	0.4041 (3)	0.0293 (3)	0.3510 (3)	4.67 (7)
C4	0.3026 (3)	0.0455 (2)	0.2979 (3)	3.87 (6)
C5	0.2892 (2)	0.1204 (2)	0.2311 (2)	3.02 (5)
C6	0.1846 (2)	0.1340 (2)	0.1577 (2)	3.09 (5)
C7	0.1907 (2)	0.0717 (2)	0.0307 (2)	2.63 (5)
C8	0.1384 (2)	−0.0292 (2)	−0.0058 (2)	3.17 (5)
C9	0.1493 (2)	−0.0980 (2)	−0.1144 (3)	3.51 (6)
C10	0.2139 (2)	−0.0687 (2)	−0.1897 (2)	3.29 (5)
C11	0.2649 (2)	0.0314 (2)	−0.1560 (2)	2.82 (5)
C12	0.2536 (2)	0.1032 (2)	−0.0470 (2)	2.38 (4)
C13	0.3101 (2)	0.2119 (2)	−0.0239 (2)	2.37 (4)
C14	0.2911 (2)	0.4012 (2)	−0.0421 (2)	2.95 (5)
C15	0.2457 (2)	0.2872 (2)	−0.0943 (2)	2.48 (5)
C16	0.1239 (2)	0.2838 (2)	−0.0854 (2)	2.55 (5)
C17	0.0703 (2)	0.2426 (2)	−0.1934 (2)	2.71 (5)
C18	0.1460 (2)	0.2225 (2)	−0.2831 (2)	2.92 (5)
C19	0.2468 (2)	0.2492 (2)	−0.2290 (2)	2.76 (5)
C20	0.3222 (4)	0.5723 (3)	−0.0706 (4)	7.6 (1)
C21	0.4266 (2)	0.2079 (2)	−0.0499 (2)	2.62 (5)
C22	0.5916 (2)	0.1197 (2)	−0.0374 (3)	4.20 (7)
C23	0.0661 (2)	0.3209 (2)	0.0216 (2)	2.93 (5)
C24	0.0702 (3)	0.4382 (3)	0.2122 (3)	5.69 (8)
C25	−0.0474 (2)	0.2107 (2)	−0.2194 (2)	3.19 (5)
C26	−0.2250 (3)	0.2708 (4)	−0.2441 (4)	6.7 (1)
C27	0.1182 (2)	0.1830 (2)	−0.4139 (2)	3.88 (6)
C28	−0.0252 (4)	0.1267 (4)	−0.5676 (3)	7.6 (1)
C29	0.3447 (2)	0.2364 (2)	−0.2959 (2)	3.13 (5)
C30	0.4612 (3)	0.3235 (3)	−0.3866 (4)	7.20 (9)
C31	0.1702 (4)	0.5784 (5)	0.5793 (5)	8.0 (1)
F1	0.0869 (2)	0.5963 (3)	0.5088 (3)	10.6 (1)
F2	0.1698 (3)	0.4789 (3)	0.5743 (5)	16.0 (1)
F3	0.1523 (3)	0.6346 (4)	0.6904 (3)	13.0 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Another analogy between the behavior of the BP-containing compounds and that of the complexes seen previously[8] resides in the possibility of decreasing the thermal stability of the mono-inserted products. Indeed, the depalladation reaction affording heterocyclic compounds occurred also in the case of such iodide substituted cyclopalladated complexes.[8] It is, however, important to note that, contrary to our observations in the preceding paper, the cationic heterocycle associated with an iodide ion was not decomposed during the reaction. Indeed only relatively small amounts of the heterocycle having Pd_2I_6 as a dianion were formed.

The most important feature that this six-membered cyclopalladated ring displays in the reactions with two alkynes per Pd atom resides in the formation of unprecedented spiro compounds. Although the expected ten-membered organopalladium ring that should have been formed by insertion of two alkynes moieties into the Pd–C bond of 1 has never been observed, we believe that it is the most likely intermediate in the synthesis of the new ligand. A likely mechanism for the formation of the spiro unit from this hypothetical ten-membered ring has been proposed recently.[13] It involves a nucleophilic attack of the carbon σ-bonded to Pd in this intermediate on the ortho carbon atom of the benzyl ring of the BP ligand. It is worth mentioning that other spiro compounds have already been synthesized via organopalladium routes.[21] In these cases, it was shown that the spirocyclization occurred similarly through an intramolecular nucleophilic attack which took place at a carbon atom that was part of an allyl unit η^3-bonded to Pd.

Scheme I. Proposed Intermediates in the Formation of Compound 6 (S = CH_3CN or H_2O; E = CO_2Me)



For the first time in the chemistry of such cyclometalated amines, the use of a palladated benzylpyridine derivative has allowed us to insert three alkyne units into its Pd–C bond. Indeed, a stoichiometric reaction has occurred when we reacted the cationic complex **2e**** with two molecules of DMAD to afford quantitatively compound **6**.[22] The formation of this latter compound can be rationalized by the formation of a 12-membered metallocycle in an early step of the reaction. This intermediate is shown in Scheme I.

The vinylic carbon–carbon double bond that is now π-bonded to Pd should be the one linked to the benzyl ring. This hypothesis is based on symmetry considerations within the 12-membered metallocyclic intermediate and also because it explains why the nucleophilic attack of the carbon σ-bonded to Pd occurs precisely at this position.[23] The existence of a carboxylate group at the carbon β to the Pd atom, which is then able to coordinate to the metal via the oxygen atom of the carbonyl group, must play an

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(21) (a) Godleski, S. A.; Meinhart, J. D.; Miller, D. J.; van Wallendael, S. *Tetrahedron Lett.* **1981**, *22*, 2247. (b) Godleski, S. A.; Valpey, R. S. *J. Org. Chem.* **1982**, *47*, 381. (c) Godleski, S. A.; Heacock, D. J.; Meinhart, J. D.; van Wallendael, S. *J. Org. Chem.* **1984**, *48*, 2101. (d) Stanton, S. A.; Felman, S. W.; Parkhurst, C. S.; Godleski, S. A. *J. Am. Chem. Soc.* **1983**, *105*, 1964.

(22) While this paper was being prepared, a similar result was published concerning a cationic derivative of cyclopalladated 8-methylquinoline and 3-hexyne: Wu, G.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1986**, *5*, 1922.

(23) For related tris-insertion reactions of alkynes into Pd–C or P–Cl bonds see: Maitlis, P. M. *J. Organomet. Chem.* **1980**, *200*, 767.

important role in the stabilization of the resulting molecule.

The behavior of the cyclopalladated complexes described in this paper allows us to define more precisely the limitation of the syntheses of heterocycles through the reactions of alkynes with these organometallic compounds. We have indeed shown here that the 10- or 12-membered metallocyclic units that were proposed as intermediates do not lead to carbon–nitrogen bond formation in opposition to smaller such moieties because they rearrange, to afford stable organometallic compounds, through intramolecular carbon–carbon bond formations. We therefore suggest, according to the preceding paper,[8] that the limit size of the intermediate organometallic rings that might lead to heterocyclic compounds should not exceed nine atoms.

Experimental Section

Details of the experimental procedure used throughout this work including reagents and physical measurements have been described in the preceding paper.[8]

Syntheses. All solvents were dried and distilled under nitrogen prior to use; cyclopalladated compound 1, formed from 2-benzylpyridine, is prepared by the published method.[9b] The iodocyclopalladated complexes were obtained by metathesis of the chloro products with an excess of sodium iodide in acetone.[8]

$[\{Pd(C(R^2){=}C(R^1)C_6H_4CH_2C_5H_4N)(\mu\text{-}Cl)\}_2]$ (2a–e). To suspensions of $[\{Pd(BP)(\mu\text{-}Cl)\}_2]$ (1) (0.31 g, 0.5 mmol) in CH_2Cl_2 (60 mL) were added stoichiometric quantities of $R^1C{\equiv}CR^2$ (1.0 mmol) (R^1, R^2 = Me, Ph, CO_2R). The mixtures were stirred at reflux temperature until the solid dissolved. The yellow solutions were taken to dryness, and the residues were washed with pentane and then dissolved in the minimum amounts of CH_2Cl_2 (ca. 10–20 mL). Addition of pentane (50 mL) afforded **2a–e** as yellow bright solids which crystallized from CH_2Cl_2/pentane at −20 °C. Analytical and spectroscopic data are given in Table I.

$[Pd\{C(R^2){=}C(R^1)C_6H_4CH_2C_5H_4N\}(C_5H_5N)Cl]$ (3a–e). An excess of pyridine (1.5 mmol) was added dropwise to the stirred solutions of **2a–e** (0.5 mmol) in CH_2Cl_2 (25 mL). Instantaneously the color of the yellow solutions changed intensities. The solvent was evaporated to dryness, and the residues were washed with pentane (2 × 10 mL). The monomers **3a–e** were precipitated quantitatively with pentane, as yellow solids, from their corresponding concentrated solutions in CH_2Cl_2 (ca. 10 mL). Compounds **3a–e** could be crystallized at −20 °C from CH_2Cl_2/pentane solutions. Their analytical and spectroscopic data are reported in Table II.

$[Pd\{(\eta^3\text{-}C_6H_4C(R^1){=}C(R^2)C(R^3){=}C(R^4))CH_2C_5H_4N\}Cl]$ (4 or 5). A mixture of $[\{Pd(BP)(\mu\text{-}Cl)\}_2]$ (1) (0.40 g, 0.64 mmol) and diphenylacetylene (0.69 g, 3.87 mmol) in CH_2Cl_2 (45 mL) was refluxed for 39 h. The orange solution obtained was evaporated in vacuo, and the residue was washed with pentane (3 × 10 mL). The remaining solid was dissolved in the minimum amount of CH_2Cl_2 and precipitated with pentane affording **4a** (0.73 g, 88%) as an orange powder. From a CH_2Cl_2/pentane solution, **4a** could be crystallized, at room temperature, as orange square crystals (50%).

The spiro compound **4a** (R^n = Ph) can be also synthesized from **2d** and C_2Ph_2 in refluxing CH_2Cl_2 (18 h). Analogous complexes **4b–f** were obtained by using a similar procedure. Reaction conditions and analytical data are reported in Table III, and spectroscopic data are given in Table IV.

Another isomer of **4a** was formed when diphenylacetylene (0.22 g, 1.23 mmol) was reacted with **2d** (0.48 g, 0.5 mmol) in refluxing chlorobenzene for 20 min. Traces of metallic palladium were removed by filtration on a Celite column (l = 4 cm). After workup, similar to that used for **4a**, **5a** was obtained as an orange solid (0.30 g, 50%) and crystallized at room temperature from a CH_2Cl_2/pentane solution.

^{13}C NMR ($CDCl_3$): **4a**, 124.8 and 121.8 (C^4 or C^5), 102.8 (C^2), 72.7 (C^6), 59.0 (C^3), 43.4 ppm (CH_2); **5a**, 101.4 (C^4), 66.0 (C^6), 59.9 (C^3), 43.4 ppm (CH_2). For other characteristic data see Tables III and IV.

$[Pd\{C(CO_2Me){=}C(CO_2Me)C_6H_4CH_2C_5H_4N\}(MeCN)_2]SO_3CF_3$ (2e).** A solution of $[\{Pd(BPMeO_2CC{=}CCO_2Me)(\mu\text{-}Cl)\}_2]$ (**2e**) (0.35 g, 0.38 mmol) in CH_2Cl_2 (15 mL) was added to a solution of $AgSO_3CF_3$ (0.20 g, 0.77 mmol) in CH_2Cl_2/MeCN (10 mL/1.5 mL). The solution was then immediately filtered on a Celite column (l = 3 cm) to remove the AgCl formed. The pale yellow solution thus obtained was concentrated under reduced pressure (to 2 mL); pentane (20 mL) was added, and the mixture was vigorously stirred until a cream solid precipitated. This solid was washed with pentane (20 mL) affording compound **2e**** (0.44 g, 87%). This was not purified further and contained one molecule of water: its presence in **2e**** could result from the fact that $AgSO_3CF_3$ was weighed in air without precaution.

Compound 2e**: ^1H NMR ($CDCl_3$) 8.81 (dd, 1 H, H_o, $^3J_{H_o\text{-}H_m}$ = 4.4 Hz), 7.79 (td, 1 H, H_p, $^3J_{H_m\text{-}H_p}$ = 7.7), 4.26 and 4.11 (2d, 2 H, CH_2, $^2J_{H_A\text{-}H_B}$ = 16.1 Hz), 3.74 and 3.68 (2s, 6 H, OCH_3), 2.25 and 2.02 (2s, 6 H, CH_3CN), 1.88 ppm (s (br), 2 H, H_2O).

$[Pd\{C(CO_2Me)(C(CO_2Me)C(CO_2Me){=}C(CO_2Me)C(CO_2Me){=}C(CO_2Me))C_6H_4CH_2C_5H_4N\}(H_2O)]SO_3CF_3$ (6). To a solution of $[Pd(BPMeO_2CC{=}CCO_2Me)(MeCN)_2]SO_3CF_3$ (**2e****) (0.44 g, 0.67 mmol) in chlorobenzene (40 mL) was added dimethyl acetylenedicarboxylate (DMAD) (0.23 g, 1.63 mmol). The reaction mixture was heated (at 126 °C) for 0.5 h; the light orange solution thus obtained was allowed to cool to room temperature. The volume of the solvent was reduced under vacuum (to 1 mL). Addition of hexane (2 × 10 mL) leads to a quantitative formation of a yellow solid (**6**) which was collected by filtration and washed with hexane (2 × 10 mL). Compound **6** was isolated in pure form (checked by ^1H NMR) (0.58 g, >99%). At room temperature, from a CH_2Cl_2/pentane solution, complex **6** could be obtained as yellow crystals.

Compound 6: IR (KBr) $\nu_{C=O}$ 1725 (br), ν_{CF} 1250 (br) cm^{-1}; ^1H NMR ($CDCl_3$) 8.59 (dd, 1 H, H_o, $^3J_{H_o\text{-}Hm}$ = 5.4 Hz), 7.64 (td, 1 H, H_p, $^3J_{H_p\text{-}H_m}$ = 7.6 Hz), 5.95 and 4.04 (2d, 2 H, CH_2, $^2J_{H_A\text{-}H_B}$ = 12.9 Hz), 4.12, 4.01, 3.90, 3.73, 3.68, and 3.65 (6s, 18 H, OCH_3), 1.74 ppm (s, 2 H, H_2O). Anal. Calcd for $C_{31}H_{30}F_3NO_{16}PdS$: C, 42.89; H, 3.48; N, 1.61. Found: C, 43.03; H, 3.13; N, 1.53.

$[\{C(Ph){=}C(Ph)C_6H_4CH_2C_5H_4N\}_2]Pd_2I_6$ (7a) and $[C(Ph){=}C(Ph)C_6H_4CH_2C_5H_4N]I$ (8a). A slight excess of diphenylacetylene (0.14 g, 0.77 mmol) was reacted with $[\{Pd(BP)(\mu\text{-}I)\}_2]$ (1) (0.24 g, 0.30 mmol) in refluxing chlorobenzene (40 mL) for 0.5 h. The black solution thus obtained was filtered on a Celite column (l = 4 cm) to remove the metallic palladium. The solvent was removed, and the purple residue was washed with pentane (2 × 10 mL). From a CH_2Cl_2 (15 mL) solution, compound **7a** crystallized as deep purple crystals (0.06 g, 36% based on iodine) by slow diffusion of pentane (10 mL) after 24 h at room temperature. The mother liquor was reduced in volume under vacuum, and **8a** was then precipitated with pentane as an orange solid (0.08 g, 43%). Compound **8a** could be crystallized from CH_2Cl_2/pentane solution (0.05 g, 25%).

Compound 7a: ^1H NMR (CD_3CN) 8.54 (dd, 1 H, H_0, $^3J_{H_o\text{-}H_m}$ = 5.4 Hz), 8.42 (td, 1 H, H_p, $^3J_{H_p\text{-}H_m}$ = 7.9, $^4J_{H_p\text{-}H_o}$ = 1.4 Hz), 8.17 (dd, 1 H, $H_{m'}$, $^3J_{H_m{'}\text{-}Hp}$ = 7.9, $^4J_{H_m{'}\text{-}H_m}$ = 1.1 Hz), 4.70 and 4.59 ppm (2 d, 2 H, CH_2, $^2J_{H_A\text{-}H_B}$ = 13.8). Anal. Calcd for $C_{26}H_{20}I_3NPd$: C, 37.46; H, 2.42; N, 1.68. Found: C, 37.81; H, 2.41; N, 1.84.

Compound 8a: ^1H NMR ($CDCl_3$) 8.81 (dd, 1 H, H_o, $^3J_{H_o\text{-}H_m}$ = 6.6, $^4J_{H_o\text{-}H_p}$ = 1.1 Hz), 8.73 (dd, 1 H, $H_{m'}$, $^3J_{H_m{'}\text{-}H_p}$ = 8.1, $^4J_{H_m{'}\text{-}H_m}$ = 1.2 Hz), 8.39 (td, 1 H, H_p, $3J_{H_p\text{-}H_m}$ = 7.8 Hz), 5.08 and 4.47 ppm (2d, 2 H, CH_2, $^2J_{H_A\text{-}H_B}$ = 13.5 Hz). Anal. Calcd for $C_{26.4}H_{20.8}INCl_{0.8}$ (**8a** + $0.4CH_2Cl_2$): C, 62.49; H, 4.10; N, 2.76. Found: C, 62.21; H, 4.19; N, 2.78. (The amount of CH_2Cl_2 vs. **8a** has been determined by ^1H NMR.)

$[\{C(Ph){=}C(CO_2Et)C_6H_4CH_2C_5H_4N\}_2]Pd_2I_6$ (7b). A solution of **2a*** (derived from **2a** by metathesis of chloride by iodide) (0.37 g, 0.32 mmol) in chlorobenzene (35 mL) was refluxed for 0.5 h. The dark solution was filtered through a Celite column, and the deep green-red solution was pumped dry. The remaining solid was washed with pentane (2 × 5 mL). The residue thus obtained was dissolved in a minimum amount of CH_2Cl_2, which with pentane gave, at room temperature, **7b** as deep purple crystals (0.07 g, 42% based on iodine). An unidentified green solid could be precipitated by addition of pentane to the mother liquor.

Compound 7b: IR (KBr) $\nu_{C{=}O}$ 1715 (vs) cm^{-1}; ^1H NMR (CD_3CN) 8.49 (td, 1 H, H_p, $^3J_{H_m-H_p}$ = 9.3 Hz), 8.33 (dd, 1 H, H_o, $^3J_{H_o-H_m}$ = 6.8 Hz), 8.19 (d, 1 H, $H_{m'}$, $^3J_{H_{m'}-H_p}$ = 8.3 Hz), 4.68 and 4.23 (2d, 2 H, CH_2, $^2J_{H_A-H_B}$ = 1.38 Hz), 4.06 (m, 2 H, OCH_2, ABX_3 spin system), 0.92 ppm (t, 3 H, CH_3). Anal. Calcd for $C_{23}H_{20}I_3NO_2Pd$: C, 33.30; H, 2.43; N, 1.69. Found: C, 33.45; H, 2.06; N, 1.63.

Collection of X-ray Data and Structure Determination. Cell constants and other pertinent data are presented in Table VIII for compounds **3″a**, **4a**, and **6**. Intensity data were collected on a Nonius CAD4 diffractometer. Corrections for Lorentz and polarization effects were applied but not for absorption, owing to the low value of the linear absorption coefficient.

The structures were solved on a PDP 11-60 computer with the Enraf-Nonius package.[8] The atomic positions of the independent atoms of the molecules were found with program MULTAN and subsequent Fourier difference synthesis.

For compounds **4a** and **6**, after the refinement of the coordinates and thermal parameters, first isotropic and then anisotropic of the non-hydrogen atoms, the positions of the hydrogen atoms were calculated. Their introduction into the refinement with fixed coordinates and isotropic thermal parameters of 5 Å^2 was significant, leading to the R and R_ω values given in Table VIII after the two last cycles of refinement of coordinates and anisotropic thermal parameters of the non-hydrogen atoms.

For compound **3″a**, after the refinement of coordinates and isotropic thermal parameters a Fourier difference synthesis revealed residual peaks assigned to two molecules of solvent, dichloromethane and toluene, respectively. Best refinement was obtained with 0.5 molecule of CH_2Cl_2 and 0.5 molecule of $C_6H_5CH_3$ per asymmetric unit. For the dichloromethane molecule, the atom C12 was placed in general position 8f of the space group $C2/c$ and C30, with an occupancy factor of 0.5, in particular position 4e. The toluene molecule is statistically distributed over two sites related by an inversion center at $^1/_4$, $^3/_4$, $^1/_2$ giving only five independent carbon atoms: C31 and C33 with occupancy factors of 1 and C32, C34, and C35 with occupancy factors of 0.5. Because of this order the hydrogen atoms were not introduced into the refinement. Refinement of the coordinates and thermal parameters (anisotropic for the 37 atoms of compound **3″a** including C12 and C30 and isotropic for C31 to C35) led to the final values of R and R_ω given in Table VIII.

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Registry No. **1**, 105369-55-9; **1***, 109996-96-5; **1****, 109997-17-3; **2a**, 109996-97-6; **2a***, 109997-18-4; **2b**, 109996-98-7; **2c**, 109996-99-8; **2d**, 105784-29-0; **2d****, 109997-15-1; **2e**, 110044-15-0; **2e****, 109997-14-0; **2f**, 109997-00-4; **3a**, 109997-01-5; **3′**a, 109997-13-9; 3″a, 109997-19-5; **3b**, 109997-02-6; **3c**, 109997-03-7; **3d**, 105813-62-5; **3e**, 105813-63-6; **3f**, 109997-04-8; **4a**, 105784-31-4; **4a***, 109997-20-8; **4b**, 110013-97-3; **4c**, 109997-05-9; **4d**, 109997-06-0; **4e**, 109997-07-1; **4f**, 109997-08-2; **4g**, 109997-09-3; **5a**, 105784-32-5; **5a***, 110013-98-4; **6**, 109997-11-7; **7a**, 109997-12-8; **7b**, 109997-22-0; **8a**, 109978-95-2; **8′**a, 109978-97-4; $PhC\equiv CCO_2Et$, 2216-94-6; $PhC\equiv CCO_2Me$, 4891-38-7; $MeC\equiv CPh$, 673-32-5; $PhC\equiv CPh$, 501-65-5; $MeOCOC\equiv CCO_2Me$, 762-42-5; $MeC\equiv CMe$, 503-17-3.

Supplementary Material Available: Tables of thermal parameters, bond distances and angles including all atoms, and least-squares planes for **3″a**, **4a**, and **6** (17 pages); listings of observed and calculated structure factors for **3″a**, **4a**, and **6** (87 pages). Ordering information is given on any current masthead page.

Reactions of Yttrium–Carbon Bonds with Active Hydrogen-Containing Molecules. A Useful Synthetic Method for Permethylyttrocene Derivatives

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Reactions of the permethylyttrocene compounds $Cp^*_2YCH(SiMe_3)_2$ (**1**) and $Cp^*_2YMe{\cdot}THF$ (**2**) with a variety of active hydrogen-containing substrates are reported. With HCl the known complexes $(Cp^*_2YCl)_2$ and $Cp^*_2YCl{\cdot}THF$ are formed. Reaction with 2,4-pentadione gives $Cp^*_2Y(acac)$ (**3**). Alcoholysis of **1** in Et_2O gives alkoxides $Cp^*_2YOR{\cdot}OEt_2$ (**4**, R = Me; **5**, R = Et; **6**, R = *i*-Pr). In the reactions with α-alkynes alkynyl complexes $Cp^*_2YC\equiv CR{\cdot}OEt_2$ (**7a**, R = Me; **8**, R = Ph; **9**, R = $SiMe_3$) are formed. When **2** reacts with propyne, $Cp^*_2YC\equiv CMe{\cdot}THF$ (**7b**) is isolated. Reaction of **1** with excess of α-alkynes in nonpolar solvents shows a regioselective, catalytic dimerization to 1-en-3-ynes. Both **1** and **2** metalate pyridines at the α-position to give $Cp^*_2Y(\eta^2\text{-}NC_5H_4)$ (**13**) from **1** and $Cp^*_2Y(\eta^2\text{-}NC_5H_4){\cdot}THF$ (**14**) and $Cp^*_2Y(\eta^2\text{-}NC_5H_3\text{,6-Me})$ (**15**) from **2**. Thermolysis of **1** in mesitylene gives the complex $Cp^*_2YDMB^1$ (**16**), which reacts with THF to form $Cp^*_2YDMB{\cdot}THF$ (**17**). The hydrides $(Cp^*_2YH)_2$ (**18**) and $Cp^*_2YH{\cdot}THF$ (**19**) are synthesized by hydrogenolysis of **1** and **2**, respectively. The hydride **19** is a catalyst in H/D exchange reactions between sp^3-CH and sp^2-CD bonds.

Introduction

The last decade has shown a dramatic and interesting development of the organometallic chemistry of group 3 and 4f elements.[2]

We recently reported the synthesis of the new monomeric permethylyttrocenes[1] $Cp^*_2YCH(SiMe_3)_2$ (**1**)[3] and $Cp^*_2YMe{\cdot}THF$ (**2**).[4] The main objective of these synthetic

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[1] In this paper the following abbreviations are used: Cp = η^5-C_5H_5; Cp′ = η^5-C_5H_4Me; Cp* = η^5-C_5Me_5; Fv* = η^1,η^5-$C_5Me_4CH_2$; DMB = η^1-3,5-dimethylbenzyl.

[2] For recent reviews see, for example: (a) Schumann, H. *Angew. Chem.* **1984**, *96*, 493. (b) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*. (c) Watson, P. L.; Parshal, G. W. *Acc. Chem. Res.* **1985**, *18*, 51.

[3] Den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Spek, A. L.; Kojić-Prodić, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726.