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Controlled Synthesis of Heterocyclic Compounds through Ring Enlargement by Alkyne Insertions into the Pd–C Bonds of Cyclopalladated Amines Followed by Subsequent Ring Closure[1]

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The chloride-bridged dimer $[\{Pd(dmba)(\mu\text{-}Cl)\}_2]$ (1) (dmba = $C_6H_4CH_2NMe_2$, 2-((dimethylamino)methyl)phenyl) reacted with 1 equiv per Pd atom of disubstituted alkynes ($R^1C{\equiv}CR^2$ in which R^1 and/or R^2 = CO_2R, where R = Me or Et) to afford regiospecifically $[\{Pd(C(R^2){=}C(R^1)C_6H_4CH_2NMe_2)(\mu\text{-}Cl)\}_2]$ (**4a–c**) through insertion of the alkyne into the Pd–C bond of 1. Compounds **4a–c** underwent a further ring expansion by insertion of a second alkyne to give the monomers $[Pd\{C(R^4){=}C(R^3)C(R^2){=}C(R^1)C_6H_4CH_2NMe_2\}Cl]$ (**6a–j**). The compound $[Pd\{C(Ph){=}C(Ph)C(Ph){=}C(Ph)(8\text{-}mq)\}Cl]$ (**7**) (8-mq = $CH_2C_9H_6N$, 8-quinolylmethyl) rearranged in boiling chlorobenzene to afford $[Pd\{C(Ph){=}C(Ph)CH(Ph)C(Ph){=}CHC_9H_6N\}Cl]$ (**8**), via a 1,3-hydrogen shift of the CH_2 group on the adjacent olefinic bond, together with trace amounts of $[\{C(Ph)C(Ph){=}C(Ph)C(Ph)CH_2C_9H_6N\}_2]Pd_2Cl_6$ (**9α**), which has been fully characterized by an X-ray diffraction study. It shows that the organic moiety of this salt is a cationic heterocycle in which C–C and C–N bonds have been formed by a depalladation process, affording a substituted cyclobutene adduct of 1*H*-benzo[*ij*]quinolizinium. Using $[\{Pd(8\text{-}mq)(\mu\text{-}I)\}_2]$ (**2***) as well as $[Pd(8\text{-}mq)(MeCN)_2]BF_4$ (**2****) as starting materials afforded good to excellent yields of cationic heterocycles **9β** and **9γ** having $Pd_2I_6^{2-}$ and BF_4^- as the counteranions, respectively. Extending these easily available ligand changes to other cyclopalladated starting materials, i.e., by substitution of chloride for iodide or with cationic derivatives, led efficiently to the synthesis of several heterocyclic products. Thus $[Pd(dmba)(MeCN)_2]BF_4$ (**1****) with diphenylacetylene afforded a quantitative yield of the product $[C(Ph){=}C(Ph)C(Ph){=}C(Ph)C_6H_4CH_2NMe_2]BF_4$ (**13**) whereas **1**** and **2**** with ethyl 3-phenylpropiolate gave the analogous heterocycles **14** and **15**, respectively, as zwitterionic species. The complex $[Pd(dmna)(MeCN)_2]BF_4$ (**3****) (dmna = $C_{10}H_6NMe_2$, 1-(dimethylamino)naphthyl-8) reacted with alkynes of the type $R^1C{\equiv}CR^2$ to afford cationic benzo[*de*]quinolizinium $[C(R^2){=}C(R^1)C_{10}H_6NMe_2]BF_4$ (**17a**, $R^1 = R^2$ = Ph; **17b**, $R^1 = CO_2Et$, R^2 = Ph). This reaction, when starting from $[\{Pd(dmna)(\mu\text{-}I)\}_2]$ (**3***), led to good yields of neutral benzo[*de*]quinolines **10a–d** via a partial demethylation of the NMe_2 group. The thermal decomposition of the monoinserted compound $[\{Pd(C(Ph){=}C(CO_2Et)C_6H_4CH_2NMe_2)(\mu\text{-}I)\}_2]$ (**4a***) led to the heterocyclic products $[\{C(Ph){=}C(CO_2Et)C_6H_4CH{=}NMe\}_2]Pd_2I_6$ (**11**) and $[C(Ph){=}C(CO_2Et)C_6H_4CH{=}N]$ (**12**). The molecular structure of compound **11** has been ascertained by means of X-ray diffraction.

Introduction

Cyclometalated compounds in which the metal–carbon σ bond is stabilized by a metal–donor atom bond are now being increasingly used for the purpose of organic synthesis. Various methods are available for the preparation of these compounds, the C–H activation reaction being one of the most widely investigated,[3] and over the past few years many studies have appeared in the literature concerning their reactivity.[4] This is due at least partly to the fact that these compounds promise to be powerful reagents for natural product synthesis.[5] The high reactivity of the metal–carbon σ bond in such transition-metal complexes leads often to facile reaction with various reagents.[6]

Emphasis has been placed on palladium(II) complexes because the Pd–C bonds in these particular compounds can undergo a large variety of "insertion" reactions with, for example, carbon monoxide,[6b,7] electron-deficient al-

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

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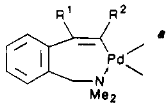
Table I. Analytical and Spectroscopic Data for Compounds 4 and 5

 [a]	anal. found[b]				IR (KBr)	
	C	H	N	yield, %	$\nu_{C=O}$, cm^{-1}	^{1}H NMR (CDCl$_3$, δ, *J* (Hz))
4a: $R^1 = CO_2Et$; $R^2 = Ph$	53.35 (53.34)	4.85 (4.89)	3.12 (3.11)	60	1690 (vs, br)	3.87 and 2.89 (m, 2 H, CH_2N), 3.74 (qd, 2 H, OCH_2), 2.69–2.32 (m, 6 H, NCH_3), 0.70 (td, 3 H, CH_3)
5a: $R^1 = CO_2Et$; $R^2 = Ph$	56.79 (56.72)	5.16 (5.10)	5.25 (5.29)	>95	1715 (vs)	8.31 (dd, 2 H, H_o, $^3J_{H_o-H_m} = 4.9$, $^4J_{H_o-H_p} = 1.5$), 7.97 (dd, 1 H, H_P, $^3J_{H_p-H_m} = 7.6$),[c] 4.17 and 3.11 (2d, 2 H, CH_2N, $^2J_{H_A-H_B} = 11.1$), 3.74 (q, 2 H, OCH_2), 3.10 and 2.91 (2s, 6 H, NCH_3), 0.69 (t, 3 H, CH_3)
4b: $R^1 = CO_2Me$; $R^2 = Ph$	52.35 (52.30)	4.45 (4.58)	3.23 (3.21)	57	1690 (vs, br)	3.85 and 2.89 (m, 2 H, CH_2N), 3.27 (s, br, 3 H, OCH_3), 2.68–2.32 (m, 6 H, NCH_3)
5b: $R^1 = CO_2Me$; $R^2 = Ph$	56.12 (55.93)	4.85 (4.85)	5.28 (5.44)	70	1710 (s)	8.27 (dd, 2 H, H_o, $^3J_{H_o-H_m} = 6.5$, $^4J_{H_o-H_p} = 1.5$), 7.91 (dd, 1 H, H_p, $^3J_{Hp-H_m} = 7.7$), 4.13 and 3.09 (2d, 2 H, CH_2, CH_2N, $^2J_{H_A-H_B} = 11.3$), 3.26 (s, 3 H, OCH_3), 3.07 and 2.89 (2s, 6 H, NCH_3)
4c: $R^1 = R^2 = CO_2Me$	43.70 (43.07)	4.37 (4.31)	3.28 (3.35)	80	1715 (vs, br)	3.83 and 2.78 (m, 2 H, CH_2N), 3.88–3.58 (m, 6 H, OCH_3), 2.95–2.42 (m, 6 H, NCH_3)
5c: $R^1 = R^2 = CO_2Me$	47.66 (48.30)	4.55 (4.62)	5.53 (5.63)	75	1722, 1705 (vs)	8.38 (dd, 2 H, H_o, $^3J_{H_o-H_m} = 5.0$, $^4J_{H_o-H_p} = 1.4$), 3.97 and 2.97 (2d, 2 H, CH_2N, $^2J_{H_A-H_B} = 11.6$), 3.61 and 3.59 (2s, 6 H, OCH_3), 2.98 and 2.84 (2s, 6 H, NCH_3)

[a] Compounds **4** refer to the chloride-bridged dimers and compounds **5** to the corresponding pyridine adduct. [b] Calculated values are given in parentheses. [c] H_o, H_m and H_p = ortho, meta, and para protons, respectively, of the pyridine.

kenes,[7j,8] acetyl or benzoyl chlorides,[7j,9] isocyanides,[10] and alkynes.[7j,11] Such "insertion" reactions are regiospecific and offer a potentially important sequence in organic synthetic methodology, particularly in the synthesis of heterocyclic compounds.[7a,8c,9b,10d,12]

It has been shown through many examples that carbonylation of cyclopalladated complexes can produce indolones,[7a] but in most of these reactions, a mixture of products was obtained. For instance, cyclopalladated benzylamine produces, on treatment with CO, 2-methylphthalimidine together with an acid zwitterion.[7a] On the other hand, there are a few other reactions with either activated alkenes,[8c,12c,e] acyl chlorides,[9b] or cyanide anions[12d] that lead to classical selective C–C bond formation followed by subsequent ring closure via C–N bond formation. These reactions, however, suffer from a lack of general applicability.

Recently, we have been interested in the reactions of these cyclopalladated complexes with alkynes and have shown that substituted alkynes[11a–c] or alkyne-like reagents as cyclopropenes[13] can formally insert into the Pd–C σ bonds of these complexes. Seven-membered ring complexes were formed by insertion of one hexafluorobut-2-yne or substituted cyclopropenes. Moreover, organometallic complexes containing nine-membered ring units have been obtained via double insertion of diphenylacetylene or 1-phenylprop-1-yne.[11a] We have also observed, though in only one case, the formation of a heterocyclic[11a] product.

These preliminary results were good evidence that these reactions might be very useful for the selective formation of C–C or even C–N bonds. However, in this respect several points merited further investigation. In this paper we wish to describe that (i) the insertion of only one alkyne into the Pd–C bond of the cyclopalladated complexes can be observed for a greater variety of alkynes (e.g., with CO_2R substituents), (ii) these new complexes, obtained by ring enlargement reactions, are still reactive toward a second alkyne insertion, so that the stepwise formation of nine-membered rings can be achieved in which two different alkynes can be incorporated, and (iii) the conditions under which heterocyclic compounds can be produced from the insertion products have now been discovered, allowing us to describe general procedures for obtaining such species regardless of the nature of the alkyne or the metalated amine in the starting material.

Results

1. Novel Alkyne Insertion in Cyclopalladated Complexes.

Previously we reported that the reaction between [{Pd(dmba)(μ-Cl)}$_2$] (**1**) and diphenylacetylene

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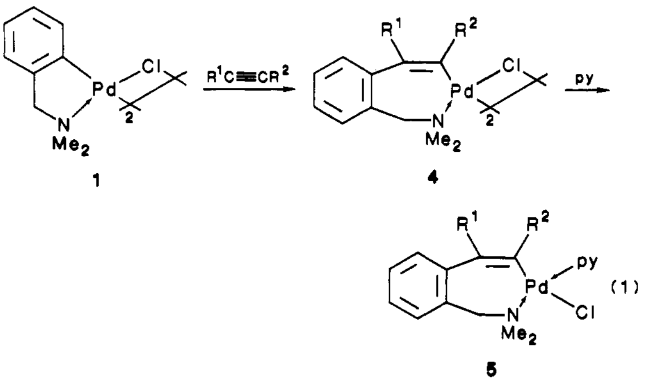
gave compounds containing a nine-membered ring via the insertion of two alkynes into the Pd–C bond of 1. Using a 2:1 ratio of the alkyne and 1 (one alkyne per Pd atom) produced a 1:1 mixture of the starting complex and the bis-inserted product.[11a] It was therefore impossible to prove that this latter was formed through the mono-inserted complex (i.e., a compound containing a seven-membered ring). In order to shed some light on this reaction, we investigated the stoichiometric reactions of 1 with a larger variety of alkynes.

1.1. Insertion of One Alkyne into the Pd–C Bond. When ethyl 3-phenylpropiolate ($PhC{\equiv}CCO_2Et$) and 1 were reacted in a 2:1 ratio at room temperature, one obtained quantitative yields of **4a**. The analytical and spectroscopic data (see Table I) indicate that one alkyne has reacted per Pd atom. The product is formulated as a seven-membered metallocyclic dimer, $[\{\overline{Pd(C(Ph){=}C(CO_2Et)C_6H_4CH_2N}Me_2)(\mu\text{-}Cl)\}_2]$ (**4a**). Its ^1H NMR spectrum shows complicated multiplets for each set of protons, suggesting that **4a** exists as a mixture of cis and trans isomers.[14]

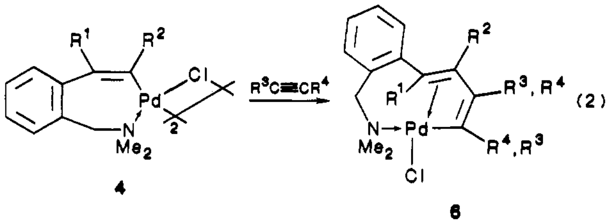
The bridge-splitting reaction of **4a** with pyridine produced quantitatively the monomeric species **5a** in which one pyridine is found per Pd. The IR spectrum indicates an intense absorption at 1715 cm^{-1} for CO_2Et. The ^1H NMR spectrum shows the diastereotopic nature of both the NMe_2 and CH_2 groups of the dmba and a triplet and a quartet assigned to one ethyl group (see Table I). These data show that **5a** is present as only one isomeric form; thus the insertion of the unsymmetric alkyne into the Pd–C bond is regiospecific. We suggest that the CO_2Et unit should be located close to the phenyl of the dmba ligand according to an X-ray structure determination of the corresponding depalladated product 11 (see later).

The corresponding reactions of 1 and methyl 3-phenylpropiolate[15] or dimethyl acetylenedicarboxylate afforded **4b** and **4c**, respectively, both of which have spectroscopic data and chemical properties close to those described for **4a** (see Table I). They too give the pyridine adducts **5b** and **5c**, and it is therefore reasonable to state that **4a**, **4b**,[16] and **4c** have similar structures.



1.2. Further Alkyne Insertion into the New Pd–C Bonds of 4. The mono-inserted dimeric compounds obtained previously from reactions of hexafluorobut-2-yne with cyclopalladated compounds have been found to be inert toward further insertion of any other alkyne.[11a] In contrast, the new seven-membered ring containing compounds, 4, readily underwent the insertion of a second alkyne molecule into their Pd–C bonds.

Indeed, compound **4a** reacted, at room temperature, with an excess of diphenylacetylene affording after workup, **6a** as orange crystals. Elemental analyses and spectroscopic data indicated that one C_2Ph_2 molecule has been added per Pd atom. In particular its ^1H NMR spectrum shows that compound **6a** exists as one single isomer and therefore the C_2Ph_2 unit must have been inserted into the Pd–C bond of **4a** producing a mononuclear nine-membered ring-containing complex. Following similar procedures, we were able to synthesize a series of compounds **6b–j**, whose analytical and spectroscopic data are reported in Table II. It can be seen from this set of reactions that the second insertion of the alkyne is not selective. All the reactions involving an unsymmetric alkyne led to mixture of two isomers. Note however, that in most of the cases they can be separated by fractional crystallization (see Table II).



Despite the fact that the dimethyl acetylenedicarboxylate could be inserted into the Pd–C bond of compound **4b** to give **6j**, it is impossible to insert this alkyne in complex **4c**. Thus the butadiene unit in these nine-membered ring containing complexes does not seem to be able to bear more than three CO_2R moieties (see compounds **6g,h,j**).

The coordination around the Pd atom is very likely to be similar to that found previously in the molecular structure of the corresponding compounds in which methyl and phenyl groups were substituting on the butadienyl unit η^3-bonded to the metal.[11a] The carbon and the nitrogen atoms are trans to each other on the metal center and the substituents R^1 and R^2 are trans on the C=C bond, π-bonded to Pd.[17] The mechanism by which the R^1 group migrates from a position cis to R^2 in 4 to the position trans in 6 is not yet fully understood, but this feature has to be kept in mind for understanding the stability of this type of compound toward the depalladation process (see later).

1.3. Reaction of $[\{Pd(8\text{-}mq)(\mu\text{-}Cl)\}_2]$ with Diphenylacetylene at Higher Temperature. We have also described previously[11a] an insertion reaction similar to those reported above between $[\{Pd(8\text{-}mq)(\mu\text{-}Cl)\}_2]$ (2) and diphenylacetylene which led, however, to poor yields of the compound 7. We have now discovered that the course of this reaction is dramatically affected by the temperature.

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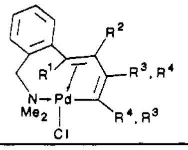
[14] It is notworthy that each cis and trans isomer can exist as two different conformers due to the nonplanarity of the metallocyclic ring. Note, however, that in opposition to the behavior of the more common five- or six-membered rings, these seven-membered cyclopalladated rings are rigid in solution on the NMR time scale, a feature that has been observed previously in related complexes.[11a,b]

[15] Compound 4b seems to be very reactive toward a second methyl 3-phenylpropiolate molecule since from a stoichiometric reaction, some amounts of a bis-inserted product was formed in a 1:1 ratio leading to an incomplete reaction.

[16] Complexes 4a and 4b are light-sensitive: when exposed to sunlight for several days, they afforded new compounds as red crystals. We were not able to characterize unambiguously these photoproducts from their spectroscopic data, and crystals suitable for an X-ray diffraction study have not yet been obtained.

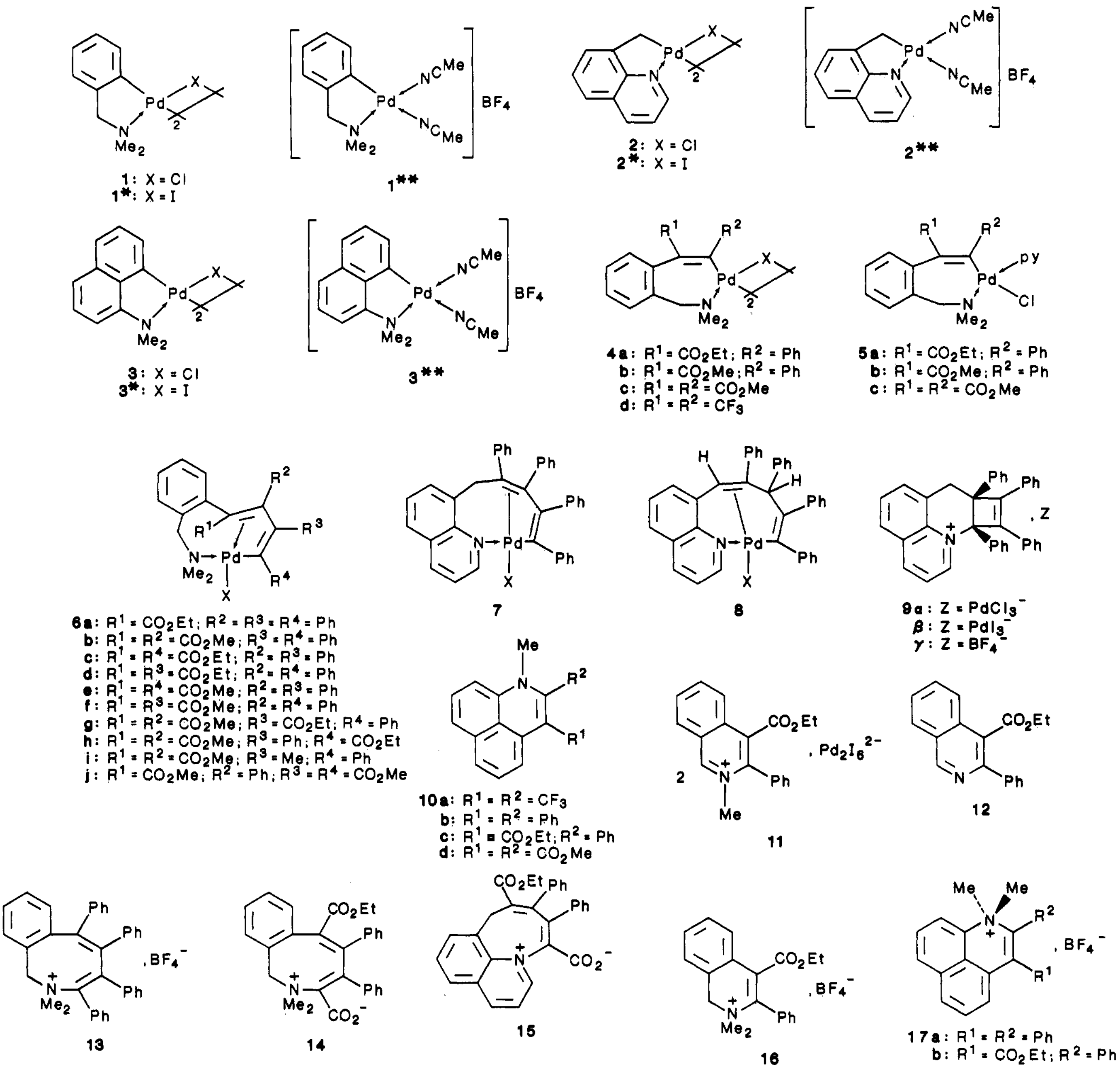
[17] The structure of compound 6i has been confirmed by an X-ray analysis which shows indeed that the $-CO_2Me$ groups are trans to each other on the C=C bond. It is noteworthy that this feature was also encountered for a rhodium compound obtained by the insertion of two C_2Ph_2 into the Rh—C bond of an ortho-metalated triphenylphosphine ligand where two of the phenyl groups were trans to each other on the C=C bond coordinated to Rh.[6c] The rationalization of the cis–trans isomerization on these alkenyl units is still being the matter of further work, and it will be published separately.

Table II. Analytical and Spectroscopic Data for Compounds 6a–j

	anal. found[a]			yield,[b] %	IR (KBr) $\nu_{C=O}$, cm^{-1}	^{1}H NMR (CDCl$_3$, δ, J (Hz))
	C	H	N			
6a: $R^1 = CO_2Et$; $R^2 = R^3 = R^4 = Ph$	64.98 (64.97)	5.20 (5.09)	2.22 (2.23)	59	1705 (vs)	4.29 (q, 2 H, OCH$_2$), 2.71 and 2.67 (2d, 2 H, CH$_2$N, $^2J_{H_A-H_B}$ = 11.0), 2.69 (s, 3 H, NCH$_3$), 2.20 (s, 3 H, NCH$_3$), 1.14 (t, 3 H, CH$_3$)
6b: $R^1 = R^2 = CO_2Me$; $R^3 = R^4 = Ph$	57.21 (56.87)	4.59 (4.61)	2.23 (2.26)[c]	60	1725 (vs)	3.75 and 3.49 (2s, 6 H, OCH$_3$), 3.72 and 3.39 (2d, 2 H, CH$_2$N, $^2J_{H_A-H_B}$ = 13.6), 2.80 and 2.37 (2s, 6 H, NCH$_3$)
6c: $R^1 = R^4 = CO_2Et$; $R^3 = R^2 = Ph$	59.66 (59.62)	5.18 (5.13)	2.22 (2.24)	48	1710, 1691 (vs)	4.30 (qd, 2 H, ABX$_3$, OCH$_2$), 3.82 (m, 2 H, ABX$_3$, OCH$_2$), 2.70 and 2.68 (2d, 2 H, CH$_2$N, $^2J_{HA-H_B}$ = 13.3), 2.69 and 2.20 (2s, 6 H, NCH$_3$), 1.21 and 0.78 (2t, 6 H, CH$_3$)
6d: $R^1 = R^3 = CO_2Et$; $R^2 = R^4 = Ph$				*d*		4.33 (m, 2 H, ABX$_3$, OCH$_2$), 4.23 (m, 2 H, ABX$_3$, OCH$_2$), 2.70 and 2.25 (2s, 6 H, NCH$_3$), 1.31 and 1.17 (2t, 6 H, CH$_3$)[e]
6e: $R^1 = R^4 = CO_2Me$; $R^2 = R^3 = Ph$	58.55 (58.40)	4.86 (4.69)	2.33 (2.35)	77[f]	1705 (br)	3.82 and 3.81 (2s, 6 H, OCH$_3$), 2.71 and 2.24 (2s, 6 H, NCH$_3$)[e]
6f: $R^1 = R^3 = CO_2Me$; $R^2 = R^4 = Ph$					1705 (br)	3.84 and 3.38 (2s, 6 H, OCH$_3$), 2.64 and 2.20 (2s, 6 H, NCH$_3$)[e]
6g: $R^1 = R^2 = CO_2Me$; $R^3 = CO_2Et$; $R^4 = Ph$	52.09 (52.71)	4.63 (4.73)	2.40 (2.36)	15	1715 (vs, br)	4.29 (m, 2 H, ABX$_3$, OCH$_2$), 3.76 and 3.48 (2s, 6 H, OCH$_3$), 3.70 and 3.37 (2d, 2 H, CH$_2$N, $^2J_{H_A-H_B}$ = 13.5), 2.82 and 2.43 (2s, 6 H, NCH$_3$), 1.32 (t, 3 H, CH$_3$)
6h: $R^1 = R^2 = CO_2Me$; $R^3 = Ph$; $R^4 = CO_2Et$				*d*	1717, 1685 (vs)	4.16 (qd, 2 H, ABX$_3$, OCH$_2$), 3.93 and 3.84 (2s, 6 H, OCH$_3$), 3.86 and 3.40 (2d, 2 H, CH$_2$N, $^2J_{H_A-H_B}$ = 13.5), 2.96 and 2.52 (2s, 6 H, NCH$_3$), 1.33 (t, 3 H, CH$_3$)
6i: $R^1 = R^2 = CO_2Me$; $R^3 = Me$, $R^4 = Ph$	57.36 (56.90)	5.16 (5.17)	2.46 (2.41)[g]	14.5[h]	1725 (vs, br)	3.80 and 3.57 (2d, 2 H, CH$_2$N, $^2J_{H_A-H_B}$ = 13.4), 3.76 and 3.62 (2s, 6 H, OCH$_3$), 2.57 and 2.49 (2s, 6 H, NCH$_3$), 1.90 (s, 3 H, CH$_3$)
6j: $R^1 = R^3 = R^4 = CO_2Me$; $R^2 = Ph$	51.93 (51.91)	4.17 (4.49)	2.41 (2.42)	90	1710 (vs, br)	3.87 (s, 3 H, OCH$_3$(R^1)), 3.85 (s, 3 H, OCH$_3$(R^3)), 3.58 (s, 3 H, OCH$_3$(R^4)), 2.80 and 2.71 (2d, 2 H, CH$_2$N, $^2J_{H_A-H_B}$ = 11.9), 2.68 and 2.21 (2s, 6 H, NCH$_3$)

[a] Calculated values are given in parentheses. [b] All the reactions occurred quantitatively. The yields reported are for isolated recrystallized product. [c] The analyses have been calculated for a molecule containing 0.25CH$_2$Cl$_2$. [d] Not isolated. The ratio of **6c**:**6d** is 3:1, of **6e**:**6f** is 3:2, and of **6g**:**6h** is 1:1 (determined by ^{1}H NMR of the crude reaction product). [e] The signals corresponding to the CH$_2$N groups overlaps with those of other protons and have not been unambiguously assigned. [f] These two isomers could not be separated; the yield refers to a mixture of **6e** and **6f**. [g] The analyses have been calculated for a molecule containing 0.5toluene. [h] The second isomer in which R^3 = Ph and R^4 = Me has not been detected in the crude reaction product.

Chart I[a]



[a] Throughout this paper we have used the nomenclature of *n* (1–8) for complexes in which X = Cl as an halogen, *n** for complexes in which X = I, and *n*** for the corresponding cationic complexes.

Indeed conducting the reaction at reflux temperature in chlorobenzene afforded after 1 h compound 7 in 80% yield.[18] In fact 7 may undergo a further transformation since if the reaction time was prolonged to ca. 3 h, another compound (8) was obtained as the major product. Elemental analyses showed that 8 and 7 have the same empirical formulas whereas their NMR spectra were significantly different. The ^{1}H NMR spectrum of 8 reveals the disappearance of the CH$_2$ protons (resonating as two doublets at 3.90 and 4.16 ppm in 7). We observed instead two singlets at 6.40 and 6.47 ppm, each signal corresponding to one proton. Moreover, the ^{13}C NMR spectrum of 8 shows only the presence of quaternary and tertiary carbon atoms. In particular a signal at 95.6 ppm and another one at 51.6 ppm are assigned to an olefinic carbon and a tertiary sp^3-carbon atom, respectively. These results can be rationalized if we consider that the π-coordinated olefinic bond in 7 has been isomerized through a 1,3-hydrogen shift from the CH$_2$ group to the adjacent carbon–carbon double bond according to eq 3. This process is well-known for coordinated olefins having allylic protons, and its mechanism is thought to involve the presence of a π-allyl metal hydride intermediate.[19]

A second product was formed during this reaction, which was obtained in low yield as red crystals 9α. The analytical data showed that the formula of 9α derived from that of 7 by addition of two chlorine atoms. The ^{1}H NMR spectrum indicates the presence of two C$_2$Ph$_2$ moieties and

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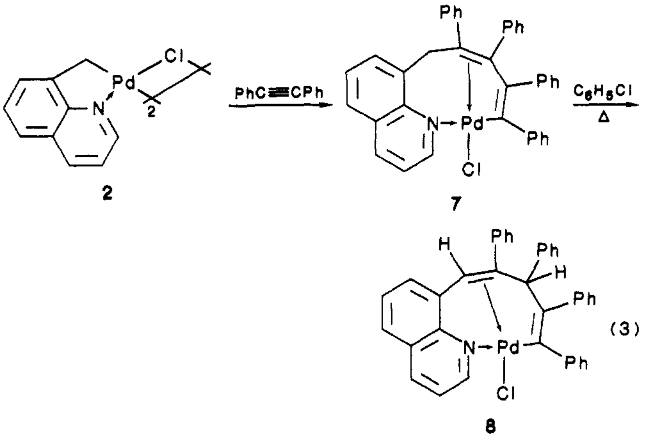
(18) The suggestion in ref 11a that compound 7 could be an intermediate in the formation of hexaphenylbenzene is unlikely. Instead, this is liable to be due to the presence of impurities in the starting complex 2.

(19) Heck, R. F. *Organotransition Metal Chemistry. A Mechanistic Approach*; Academic; New York, London 1974; p 80.

(20) Most of the remaining organic ligand was recovered as a pentane-soluble off-white material, whose formula could not be determined.



(3)

a quinoline ring. The CH_2 group is found to have two inequivalent protons at 4.12 and 5.20 ppm. In order to determine unambiguously the structure of this new molecule **9α**, an X-ray diffraction study was carried out. An ORTEP diagram of the molecular structure and selected distances and angles are shown in Figures 1 and 2.

The new molecule **9α** consists of an ionic association between two organic heterocyclic cations and a Pd_2Cl_6 dianion. It lies on a crystallographic inversion center. The Pd_2Cl_6 unit has a standard geometry. The cation can be described as being a tetrasubstituted cyclobutene adduct of a 1*H*-benzo[*ij*]quinolizinium cation. The new bonds that have been formed by the depalladation process are C11–C12 and C12–N1. However, the distance of the former is significantly longer [1.603 (4) Å] than a normal C–C single bond whereas the distance of the later is as expected for a C–N single bond: the cationic charge is therefore obviously located on the nitrogen atom. The benzo[*ij*]quinolizinium and the cyclobutene rings are fused with the cis stereochemistry, the two phenyl groups on C11 and C12 being cis to each other with respect to the four-membered ring.

2. Synthesis of Heterocycles. We have shown above how cyclopalladated complexes underwent selective insertion of alkynes leading to new organometallic complexes. In only one case (the reaction between **2** and C_2Ph_2) did we observe the formation of a heterocyclic compound (**9α**) in which the palladium is no longer directly bonded to the organic unit.

We consider this result particularily important because it is the second independent observation since we reported the first synthesis of a heterocycle[11a] by the reaction between a cyclopalladated amine and an alkyne.

We therefore decided to seek the appropriate conditions that might promote the deliberate synthesis of heterocyclic compounds. Recently, O'Sullivan and Parkins described several reactions leading to such products.[12b] These authors did in fact observe that the cyclization with CO and RNC occurred under much milder conditions than those described for related reactions using different starting materials.[7a,12] They assigned this result to the use of cyclopalladated primary amines compared to the corresponding tertiary amine ligands. However, their starting material differed also by the nature of the bridging anionic ligand since their compounds contained iodide instead of the more commonly used chloride or acetate anions.

In view of our results we have now investigated the influence of the iodide in these reactions; i.e., we have performed the reactions seen above starting from complexes containing this anion.

2.1. Role of the Iodide Ligand on the Course of the Reaction. 2.1.1. Complexes Containing the 8-Quinolylmethyl Ligand. When the reaction between **2*** and diphenylacetylene was performed, a dramatic change in the course of the reaction was observed. Indeed after 0.5 h in refluxing chlorobenzene, we obtained a very good yield of compound **9β** as purple crystals. In fact the reaction seemed to be quantitative on the basis of iodine.

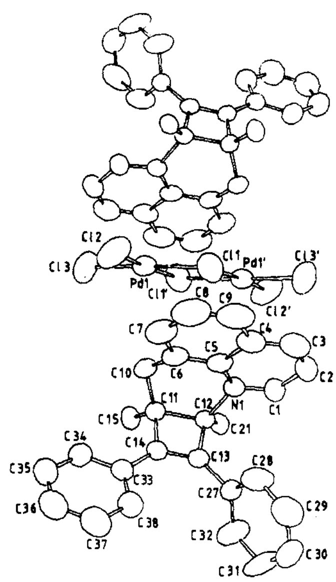


Figure 1. ORTEP view of $[\{C(Ph)C(Ph){=}C(Ph)C(Ph)CH_2C_6H_6N\}_2]Pd_2Cl_6$ (**9α**). The two phenyl groups on C11 and C12 are only represented by their ipso carbon atom for clarity: Pd–Cl(bridge) = 2.321 (1) Å; Pd–Cl(terminal) = 2.268(1) Å.

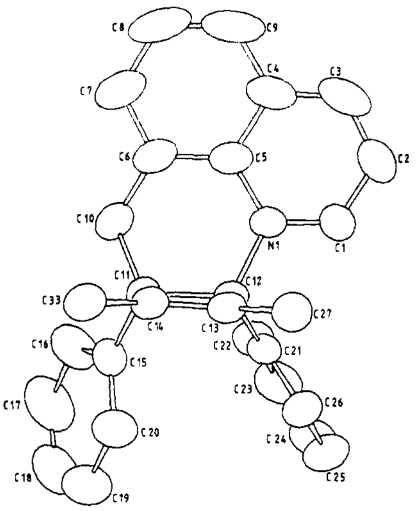
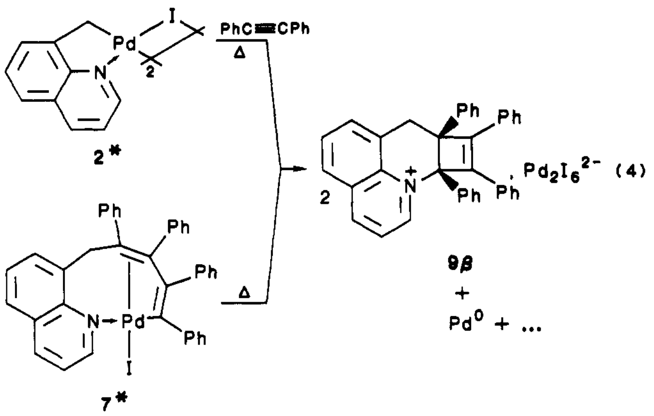


Figure 2. ORTEP view of $\{C(Ph)C(Ph){=}C(Ph)C(Ph)CH_2C_6H_6N\}$ in **9α**. The two phenyl groups on C13 and C14 are only represented by their ipso carbon atom for the sake of clarity. Selected distances (Å) and angles (deg): C11–C12 = 1.603 (4), C12–C13 = 1.529 (4), C13–C14 = 1.332 (4), C14–C11 = 1.524 (4), C12–N1 = 1.540 (3), C10–C11 = 1.527 (4). C10–C11–C12 = 113.1 (2), C12–C11–C14 = 84.3 (2), C11–C12–C13 = 85.5 (2), C5–N1–C12 = 119.9 (2), C6–C10–C11 = 114.0 (3).

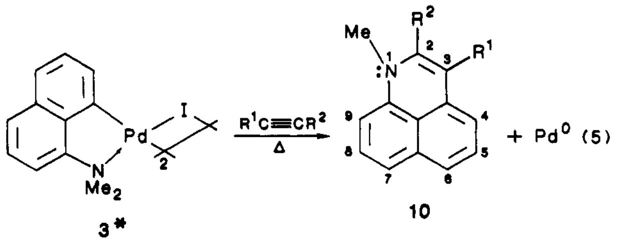
The characterization of **9β** was easily ascertained since its spectroscopic data were analogous to those of **9α**. It was possible to demonstrate that **7*** (which is derived from **7** by metathesis of chlorine for iodine) is an intermediate in the formation of **9β**. A solution of **7*** in toluene at reflux temperature gave **9β** quantitatively (again on the basis of iodine).[20] Moreover, this reaction also occurred at room temperature and could be followed in $CDCl_3$ solution by ^1H NMR, the reaction being complete after ca. 10 days.

In order to confirm the crucial role of the iodide in the ring closure process, i.e., in the C–N bond formation, we



have applied the same method to the reaction between cyclopalladated 1-(dimethylamino)naphthyl-8 (dmna) and alkynes. The choice of this $\widehat{CN}$ ligand was influenced by the fact that one cyclization reaction had already been observed with hexafluorobut-2-yne.[11a] Moreover, this complex [{Pd(dmna)(μ-Cl)}$_2$] (**3**) was totally inert toward any other alkyne; even after several days in refluxing chlorobenzene no reaction could be observed.

2.1.2. Complexes Containing the 1-(Dimethylamino)naphthyl-8 Chelate. Reaction of the iodide derivatives [{Pd(dmna)(μ-I)}$_2$] (**3***) with hexafluorobut-2-yne (hfb) indeed led to improved yields of **10a** (50%) (it was obtained in only 20% yield from the related chloride compound **3**). This starting material **3*** also reacted with the other alkynes (in comparable conditions, i.e., refluxing chlorobenzene) to afford a variety of heterocycles, **10b–d**, in excellent to reasonable yields. The Pd may be recovered quantitatively as Pd metal.



In the case of the reactions with diphenylacetylene and ethyl 3-phenylpropiolate which afforded **10b** and **10c**, respectively, we checked that these reactions were really quantitative. Indeed the ^{1}H NMR spectra of the crude products showed no other signals than those corresponding to **10b** or **10c**. These neutral heterocycles were easily characterized by their analytical and spectroscopic data (see Table III).

On the other hand, the product **10d**, formed from the reaction between **3*** and dimethyl acetylenedicarboxylate, was obtained in only 50% yield. This is due to the relative lack of selectivity of the reaction with this particular alkyne. We have observed the formation of a green product which was probably derived from the polymerization of the alkyne. A similar result was observed in the case of the reaction between hfb and **3***.

It is worth mentioning the presence in the ^{1}H NMR spectrum of each compound as a doublet at ca. 6.3 ppm for a high-field-shifted aromatic proton. This fact is likely to be consistent with the interaction of H^9 with the stereochemically active lone pair on the nitrogen[21] (see Table III). A second high-field shift occurs in the case of **10b** since another doublet is found at 6.13 ppm. This obviously results from the presence of a phenyl group at position 3 of the benzo[*de*]quinoline nucleus, and therefore the proton at position 4 should be positioned within the anisotropic cone of this phenyl ring. The product **10c** obtained from the insertion of ethyl 3-phenylpropiolate consists of two isomers in a 95:5 ratio. It is noticeable that the ^{1}H NMR spectrum of the major isomer does not display an upfield shift for H^4. Therefore it is likely that the Ph group is not found on C^3 but on C^2 close to the nitrogen atom. This regioselectivity is in agreement with our observations for the insertion of this unsymmetric alkyne into the Pd–C bond of **1**.

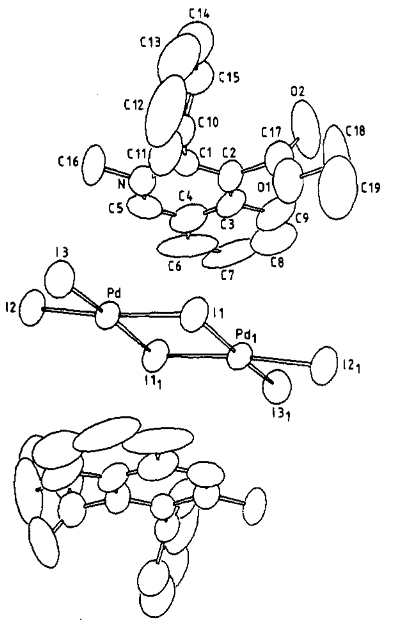


Figure 3. ORTEP view of [{$\overline{C(Ph)=C(CO_2Et)C_6H_4CH=N}Me$}$_2$]-Pd$_2I_6$ (**11**): Pd–I(bridge) = 2.592 (1) Å; Pd–I(terminal) = 2.596 (1) Å.

2.1.3. Complexes Containing the 2-((Dimethylamino)methyl)phenyl Chelate. Contrary to our previous observations, the introduction of the iodide in **1*** did not lead to the expected ring closure process when it was reacted with an excess alkynes. These reactions afforded only compounds analogous to **6**. No further reactions occurred even when compounds **6*** (in which the halogen is the iodine) were heated at reflux temperature in chlorobenzene for several hours.

However, compound **4a*** did display a completely different behavior. Indeed after 3 h in refluxing chlorobenzene a significant amount of metallic Pd was formed together with a deep red solution. This latter afforded the two products **11** and **12** which were separated by their different solubility. Compound **12** was extracted in pentane from the crude product, whereas **11** was obtained as purple crystals from a CH$_2$Cl$_2$/pentane solution.

The true formulation of **11** was ascertained by an X-ray diffraction study that shows the presence of an isoquinolinium unit (see later). The formula of the neutral organic product **12** was deduced from that of the cationic part of **11** in which the remaining methyl group on the nitrogen has been removed. The ^{1}H NMR spectra revealed only one N–Me group for **11** and no such signal is found on the spectrum of **12**. The proton ortho to the nitrogen resonates at 10.45 ppm for **11** and at 9.39 ppm for **12**. Thus, this reaction offered an original way for the preparation of an isoquinoline ring starting from a dimethylbenzylamine moiety via complete demethylation of the nitrogen atom.

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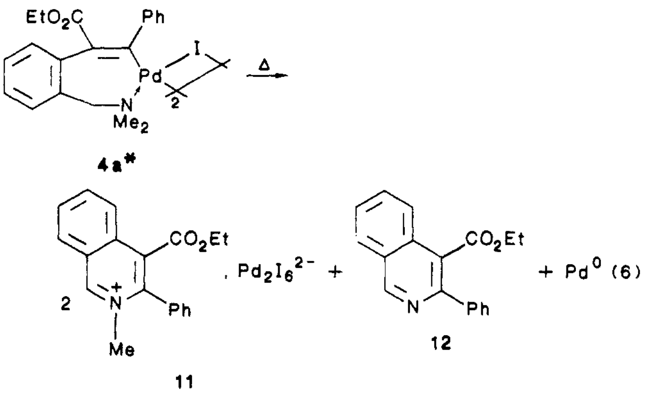
[21] The ^{1}H NMR spectra of the corresponding cationic heterocycles **17a** and **17b** (see later) show the usual resonance for this aromatic proton H^9 because, in this case, the lone pair of the nitrogen is no longer available.



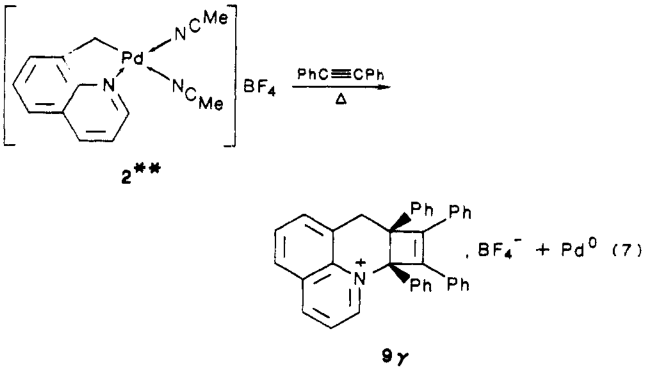
Description of the Molecular Structure of 11. The molecular structure with its numbering system is shown in Figures 3 and 4 together with selected distances and angles. Like **9α**, compound **11** consists of an association of two cationic quinolinium rings with a Pd_2I_6 dianionic unit. It also lies on a crystallographic center of symmetry. The bond lengths and angles within the nitrogen-containing heterocycle (see Figure 4) are good evidence of the aromaticity of this ring. The position of the Ph group, which is found on the C adjacent to the nitrogen atom, confirms the geometry that we proposed for the organometallic seven-membered ring in **4a**, i.e., with the CO_2Et unit on the carbon atom adjacent to the phenyl of the dmba.

2.2. Reactivity of Cationic Cyclopalladated Compounds. We have shown in the preceding section the crucial role of the nature of the anionic ligand coordinated to the metal in these cyclopalladated compounds. The replacement of chlorine by iodine had a dramatic effect not only on the reactivity of the Pd-C bonds but also on the ease of formation of the C–N bonds.

However, since most of the heterocyclic compounds thus formed are cationic ones, we thought it possible to improve both the yields and the scope of these reactions by using cationic organopalladium complexes as starting materials.

We chose cationic palladocycles in which weakly coordinated ligands are bound to the metal, in order to facilitate the coordination of the alkyne within the coordination plane of the palladium, since this is likely to be the first step in the insertion reaction.[11b]

2.2.1. Cationic Complexes Derived from the 8-Quinolylmethyl and 2-((Dimethylamino)methyl)phenyl Chelates. The compound $[Pd(8\text{-mq})(MeCN)_2]BF_4$ (**2****), when treated with diphenylacetylene in refluxing C_6H_5Cl, led to a quantitative formation of metallic palladium together with a nearly quantitative yield of the desired product **9γ**. Its formulation is confirmed by the IR and the ^1H NMR spectroscopic data. It is noteworthy that this new procedure afforded an almost quantitative yield of the organic cationic heterocycles; thus none of the palladated amine was lost during the reaction contrary to our observations for **9α** and **9β**.



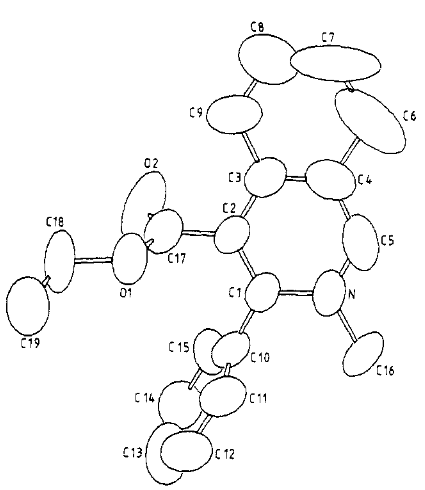
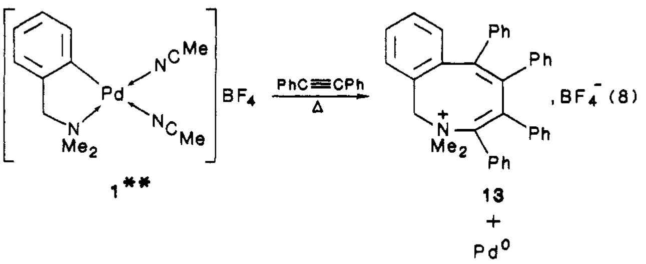


Figure 4. ORTEP view of the substituted isoquinolizinium $[\overline{C(Ph){=}C(CO_2Et)C_6H_4CH{=}N}Me]^+$ of compound 11. Selected distances (Å) and angles (deg): N–C5 = 1.23 (1), N–C1 = 1.44 (1), N–C16 = 1.48 (1); C1–N–C5 = 122.4 (8), C5–N–C16 = 118.7 (8), N–C5–C4 = 123.9 (8).

Similarly, the reaction between the palladated dmba in **1**** with diphenylacetylene gave, this time, **13** as the only product of the reaction. Its formula was confirmed by analytical data and mass spectrum. The NMe_2 group of **13** gave raise to two sharp singlets (^1H NMR) at −80 °C in C_7H_8 which coalesce at room temperature to one broad signal. This observation is easily obtained when considering that the NMe_2 unit must become diastereotopic after the new C–N bond has been formed, thus closing the heterocyclic ring, and that the molecule is not rigid in solution. We do not have any further evidence as to decide unambigously whether **13** is a cyclobutene adduct of the dmba, analogous to **9**, or whether it is an eight-membered ring with an open-chain structure. However, as most of the related compounds obtained by cycloaddition of alkynes to enamines do have an open chain structure,[22] it is very likely that **13** has the stereochemistry depicted in eq 8.



The fluxional process that renders the two diastereotopic methyl groups equivalent on NMe_2 could be of the type described in the last steps of Scheme I (see later) which involves the participation of a cyclobutenyl cation via heterolytic cleavage of the C–N bond. The nitrogen atom could thus invert its configuration before the C–N bond is re-formed.

The same reaction can be extended to other alkynes. Heating **1**** in C_6H_5Cl in the presence of ethyl 3-phenylpropiolate led to the formation of an organic product **14** as a waxy solid. Its contamination by impurities could not be prevented even after chromatography

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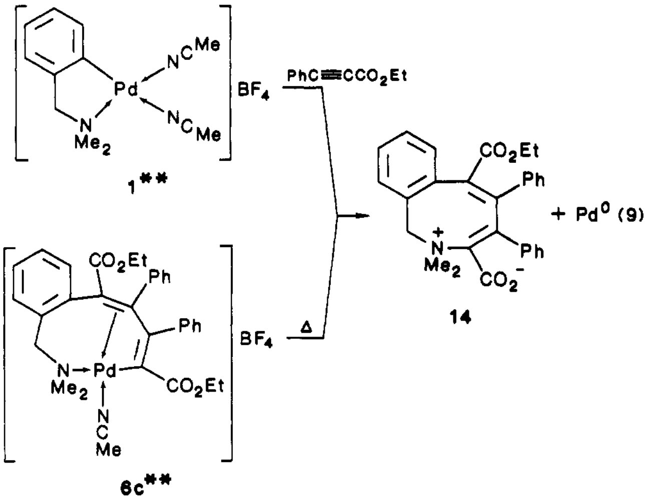
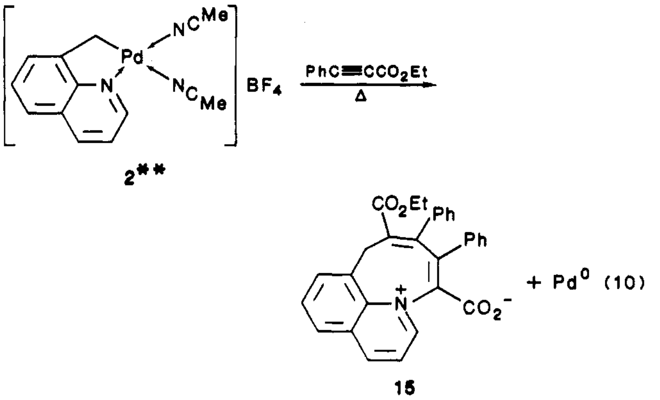
[22] (a) Lehman, P. G. *Tetrahedron Lett.* **1972**, 4863. (b) Acheson, R. M.; Paglietti, G. *J. Chem. Soc., Chem. Commun.* **1973**, 665.

on an alumina column. It was therefore characterized only from its spectroscopic features. Its IR spectrum showed the characteristic absorptions for carboxylate groups at 1720 and 1615 cm^{-1}. Its ^{1}H NMR spectrum indicated a fluxional behavior comparable to that observed for the preceding compound **13**. In addition, this spectrum revealed that two phenyl substituents were present, but there was evidence for only one ethyl group. This was also confirmed by the mass spectral data (see Experimental Section). All these indications are consistent with the formation of an eight-membered heterocycle which is followed by the cleavage of an ethyl group leading to the formation of a CO_2^- fragment. This carboxylate anion should be stabilized by the neighboring cationic charge on the nitrogen, thus giving rise to zwitterionic species, **14**.

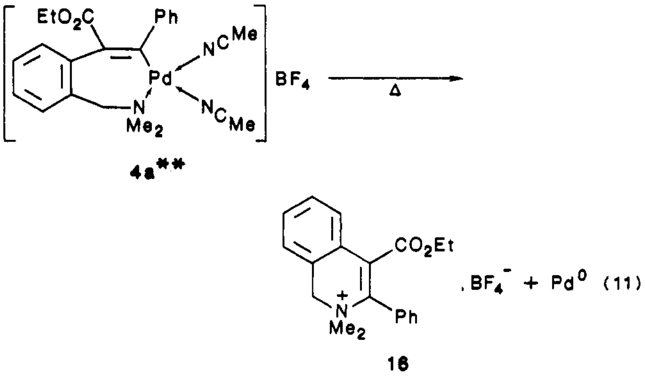


The same compound was formed by heating **6c**** (obtained by treating **6c** with $AgBF_4$/MeCN) in refluxing C_6H_5Cl. Therefore the distribution of the substituents on the butadiene unit in **14** follows the one proposed for **6c**.

The corresponding 8-mq derivative **15** was obtained from complex **2**** and the same asymmetric alkyne. Its spectroscopic data were analogous to those found for compound **14**. This result is an illustration that the use of cationic complexes as starting materials enlarges the scope of the insertion reaction since the organometallic precursor of **15** could not be obtained via **2** with the corresponding alkyne.

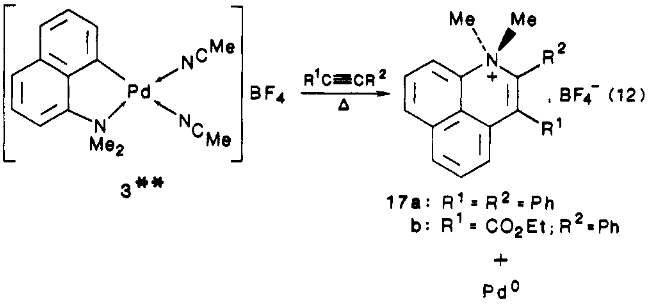


An interesting behavior of the cationic metallocycles compared to the iodide-containing ones has been observed in case of the thermal depalladation of compound **4a****. Indeed in refluxing chlorobenzene it afforded the product **16**. In contrast to the related compounds **11** and **12** both the benzylic protons and the two methyl of the NMe_2 group of the dmba ligand in **16** were still present, giving rise to cationic heterocycle as a BF_4 salt.



2.2.2. Cationic Complex Derived from 1-(Dimethylamino)naphthyl-8. We have also checked that the cationic cyclopalladate derivative of *N*,*N*-dimethylnaphthylamine $[Pd(dmna)(MeCN)_2]BF_4$ (**3****) by reaction with alkynes afforded substituted benzo[*de*]quinolinium compounds instead of the neutral corresponding heterocycles **10**. However, this reaction did not work satisfactorily in the case of hexafluorobut-2-yne: we obtained a mixture of two products that we were unable to separate. Nevertheless, the spectroscopic and mass spectral data allowed us to detect the presence of the expected cation.

On the other hand, **3**** afforded, by reaction with diphenylacetylene, the sparingly soluble heterocycle **17a** as dark purple crystals. When ethyl 3-phenylpropiolate was used, the corresponding compound **17b** was obtained, though in poorer yield.[23]



Discussion

This study provides many answers to the questions relevant to the insertion of alkynes into the Pd–C bonds of cyclopalladated tertiary amines. In the case of hexafluorobut-2-yne, the mono-inserted seven-membered palladocycle has been shown to be inert toward a second alkyne insertion,[24] whereas in the case of diphenylacetylene the mono-insertion reaction cannot be observed because the second insertion is probably more facile than the first one leading readily to the insertion of two alkynes.[11a]

Stepwise insertion of two different alkyne molecules can be achieved by varying the electron-releasing power of the substituents R^n of the alkynes. In fact, the electron-withdrawing character of R^n modulates the reactivity of the mono-inserted intermediate, so that using alkynes substituted by one or two CO_2R groups makes it feasible to observe all the possible substitutions.

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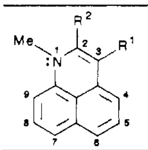
(23) The analysis of the crude product revealed the presence of **10c**; moreover, in both reactions (with diphenylacetylene and ethyl 3-phenylpropiolate) a variable amount of the starting material **3** was detected. This side reaction is obviously due to the use of a chlorinated solvent.

(24) This is, in fact, the case when the second alkyne is added in refluxing CH_2Cl_2. After submission of this paper we have found that in refluxing PhCl a second alkyne can be inserted into the Pd–C bond of $[(8\text{-mqCCF}_3{=}\text{CCF}_3)Pd(Cl)]_2$ affording a new organic heterocyclic compound: Pfeffer, M.; Le Borgne, G., unpublished results.

Table III. Analytical, Physical, and Spectroscopic Data of Compounds 10b–d

	anal. found^a				IR (KBr)	^{1}H NMR ($CDCl_3$, δ, J (Hz))			
	C	H	H	color	$\nu_{C=O}$, cm^{-1}	NMe	CO_2R	H^9	H^4
10a: $R^1 = R^2 = CF_3$ (see ref 11a)				red		3.21 (q, $^5J_{H\text{-}F}$ = 2.2)		6.35 ($^3J_{H9\text{-}H8}$ = 6.6)	
10b: $R^1 = R^2$ = Ph	89.40 (90.09)	5.78 (5.70)	4.00 (4.20)	yellow-green^b		3.87 (s)		6.23 (d, $^3J_{H9\text{-}H8}$ = 7.9)	6.13 (d, $^3J_{H4\text{-}H5}$ = 7.1)
10c: R^1 = CO_2Et; R^2 = Ph	80.37 (80.24)	5.66 (5.77)	4.17 (4.25)	yellow-green^b	1695 (vs)	3.86 (s)	3.80 (q), 0.77 (t)	6.25 (dd, $^3J_{H9\text{-}H8}$ = 7.5)	
10d: $R^1 = R^2 = CO_2Me$	68.45 (68.68)	5.24 (5.05)	4.65 (4.71)	orange	1730, 1690 (vs)	3.09 (s)	3.93 (s), 3.81 (s)	6.30 (dd, $^3J_{H9\text{-}H8}$ = 6.9)	

^{a} Calculated values are given in parentheses. ^{b} Solutions of this compound in chlorinated solvents are air-sensitive.

The insertion of the first alkyne into the Pd–C bond is highly regioselective; thus, when an unsymmetric alkyne was used, we found that the carbon bearing the more electron-withdrawing groups (e.g., CO_2R vs. Ph) is found adjacent to the previously metalated carbon atom. With the assumption that the steric requirements of CO_2R and Ph groups are comparable, the orientation of the reaction must be under electronic control. Interestingly, the same result was found for all the $\widehat{\mathrm{CN}}$ chelated amines used.[25]

The nature of the substituents on the palladium atom in the starting complexes has a dramatic effect not only upon the course of the insertion reaction but also on the stability of the organometallic compounds formed. In some cases, replacement of chlorine by iodine has markedly improved the reactivity of the Pd–C bond (see, for example, the insertion into the Pd–C bond of the dmna complexes). Moreover, the iodine-containing products are obviously much less stable than the corresponding compounds with chlorine. Indeed the 8-mq compounds and the dmna ones readily undergo the formation of a N–C bond via reductive elimination process.

Another independent ligand change on the palladium consists of using cationic starting complexes.[26] This also results in an interesting activation of the organometallic complexes. Thus in the case of the 8-mq derivative an almost quantitative yield of the heterocyclic cation could be obtained (see **9γ**), and in the case of the dmba complexes syntheses of heterocyclic products could be achieved which were impossible to obtain from iodine-containing complexes. However, for dmna complexes the use of cationic species did not afford clean reactions, although cationic heterocycles could still be obtained.

Proposed Mechanism for the Formation of Heterocyclic Products. The formation of the heterocycles can be rationalized by the reductive elimination process of the chelating ligands. Indeed in many cases we observed the nearly quantitative formation of metallic palladium except in some cases which will be discussed later (compounds **9α**, **9β**, **11**). This type of reaction is indeed very well-documented for the formation of C–C bonds from organometallic complexes.[27] To our knowledge only rare examples have been reported in the literature in which a C–N bond is formed by reductive elimination between a σ-bonded carbon and a coordinated tertiary amine. These include the carbonylation reactions of such cyclopalladated amines[7a] or the reactions of these species with isocyanides.[12b,c] In this respect, it is also worth mentioning the few C–N bond formations that have been reported between carbon and nitrogen atoms both σ-bonded to the same metal.[28]

A theoretical analysis on the mechanism of reductive elimination of d^8 organo transition-metal complexes has been published recently by Hoffman and his co-workers.[29] The main conclusions that have been drawn from this study are that (i) the elimination pathways usually proceed through three-coordinate intermediates especially for Pd(II) compounds, (ii) in the four-coordinate complex the better the σ-donating capability of the leaving groups, the more facile the elimination, and (iii) stronger σ-donor ligands trans to the leaving groups will increase the barrier to elimination by destabilizing the d orbital which is σ-antibonding with respect to the ligands.

This study is rather helpful to rationalize the different reductive elimination behavior of the cyclopalladated complexes we have used although the above conclusions were obtained from completely different systems, e.g., PdR_2L_2, where R = an alkyl and L = a phosphine.[29] The cationic complexes **1**–3**** are only weakly stabilized by acetonitrile which is well-known to be a rather labile ligand, and hence it has poor σ-donor properties. MeCN should therefore be easily displaced from Pd, leaving it three-coordinate, and moreover it does fulfill the third condition since it should decrease the activation energy that must be reached by the complexes for achieving the elimination. A further explanation for the easy depalladation reaction in the case of the cationic complexes is that in these compounds the palladium atom has been made more electrophilic than in the corresponding chloride-containing palladocycles. This not only results in an increased reactivity of the polar Pd–C bond toward nucleophiles like alkynes but also facilitates the oxidation of the organic ligand of

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[25] The same regioselectivity has been observed in the case of palladated 2-benzylpyridine. Maassarani, F.; Pfeffer, M.; Le Borgne, G., *Organometallics*, following paper in this issue.

[26] During this paper was in preparation, Heck et al. have published related observations for cyclopalladated azobenzene and shiff base ligands: Wu, G.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1986**, *5*, 1922. See also a communication on a sulfurous-containing cyclopalladated compound: Dupont, J.; Pfeffer, M. *J. Organomet. Chem.* **1987**, *321*, C13.

[27] This is actually a fondamental process of organometallic chemistry to afford C–C bond formation. See, for instance: Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic: New York, San Francisco, and London, 1978.

[28] (a) Hoberg, H.; Oster, B. W. *J. Organomet. Chem.* **1983**, *252*, 359. (b) *Ibid.* **1982**, *234*, C35. (c) Hoberg, H.; Riegel, H. J. *J. Organomet. Chem.* **1983**, *241*, 245. (d) Hoberg, H.; Sümmermann, K. *J. Organomet. Chem.* **1983**, *253*, 383. (e) *Ibid.* **1984**, *264*, 379. (f) *Ibid.* **1984**, *275*, 239.

[29] Tatsumi, K.; Hoffman, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857.

the molecule by the Pd atom.

One might argue that in the case of halide-bridged systems, tetracoordination is retained throughout the elimination process and that the above argument does not apply. Moreover I^- is usually considered as being a better σ donor than Cl^-, and we would therefore expect to have a greater barrier to elimination for I^- than Cl^-, and thus at variance with our findings. One should note, however, that an inverse *spectroscopic order*, based on d–d transition energies in substituted Cr(III) octahedral complexes, has been found experimentally[30] and rationalized by Burdett,[31] the d metal orbital being more destabilized by Cl^- than by I^-. Reasoning along the same lines in our tetracoordinated system, one therefore expects a destabilization of the d orbital which is σ-antibonding with respect to the halogen ligands greater for Cl^- than for I^-. As a result the reductive elimination should be easier for I^- than for Cl^- containing complexes.

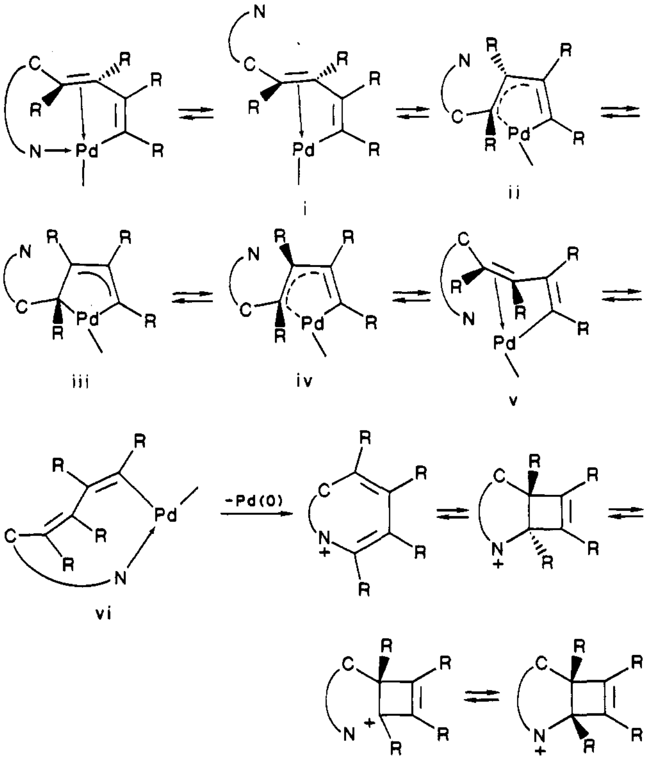
The formation of the compounds in which $Pd_2I_6{}^{2-}$ is formed as the counteranion of the cationic heterocycles can be rationalized by the following considerations: the reductive elimination of the Pd(II) in complexes containing iodide should lead to Pd metal together with the expected cationic heterocycles associated with an iodide ion.[32] In contrast to the observed stability of their $BF_4{}^-$ homologues, these heterocycles are only weakly stabilized by I^-. Depending on the amine used, several degradations can be observed. In the case of 8-mq this reaction led to an unidentifiable material, as far as the organic cation is concerned, whereas some kind of concerted reaction must occur between the iodide anion thus generated and the Pd(II) still present in the reaction leading to $Pd_2I_6{}^{2-}$ units. This latter dianion is then able to stabilize the heterocyclic cations that have not yet decomposed.

When the C͡N chelate is the dmba, the heterocyclic cation formed at an early stage of the reaction should be the same than that found in compound **16** but associated with I^- instead of the $BF_4{}^-$ anion. This compound is again obviously not stable, and it leads to degradation reactions similar to that described above, but this time most of the organic heterocycle is recovered as stable isoquinoline derivatives in **11** and **12**. Similarly, when C͡N is the dmna ligand, the formation of the neutral compounds **10** should be formed quantitatvely by the loss of methyl iodide from the corresponding cationic intermediates.

With the assumption that the organometallic complexes have been activated by the presence of a cationic charge on Pd or by the substitution of Cl^- for I^- ligands, the formation of the six-membered heterocycles **10**, **11**, **12**, **16**, or **17** can be easily explained by the reductive elimination of Pd from the corresponding seven-membered organometallic intermediates in which one alkyne has been inserted into the Pd–C bond of the starting materials **1** or **3**. In these complexes, the carbon and the nitrogen atoms are cis to each other: two electrons are transferred from the C͡N chelate to the palladium center via an intramolecular redox reaction leading to palladium metal. This is followed in the most general cases by the production of a cationic heterocycle by subsequent bond formation between the carbon and the nitrogen.

The reaction path by which the carbon–nitrogen bond is formed to afford compounds **9**, **13**, **14**, and **15** should be less straightforward because here the organometallic intermediate in which two alkynes have been inserted into the Pd–C bond of **1** or **2** do not have the required stereochemistry for the depalladation to occur. Indeed in compounds **6** and **7** the carbon and the nitrogen atoms are located trans to each other on the Pd center, a situation that precludes the intramolecular formation of a C–N bond via a reductive elimination process. Moreover the R^1 and R^2 substituents in compounds **6** are trans to each other with respect to the carbon–carbon double bond that is π-bonded to Pd; in the heterocyclic compounds **13** and **14**, which are made from **6**, the R^n substituents must be cis to each other on the butadienyl chains that link the carbon and the nitrogen atoms of the dmba unit in order to lower the tension that would otherwise exist within the heterocyclic eight-membered ring.

Scheme I



A likely reaction path, which leads to the formation of an intermediate having the desired geometry, has thus been drawn in Scheme I. The first process of this reaction sequence involves the decoordination of the nitrogen atom to form three-coordinate Pd complexes. This intermediate (i) could then experience a stereomutation to the intermediate (v) via a metallocyclic flip which requires the formation of a metallacyclopentenyl intermediate (iii). This mechanism has been proposed earlier by Taylor and Maitlis[33] for explaining the behavior of a related palladium compound in which two adjacent R groups on a η^3-butadienyl unit isomerized from trans to cis. This reaction path might however only be operative for the compounds in which the C͡N moiety is dmba. There is indeed an obvious difference in reactivity between these later compounds and those containing the 8-mq chelate which leads to much easier depalladation reactions even at room temperature. As suggested by molecular models the geometry of the 8-mq-containing complexes, e.g., **7**, might well be different from that of **6** so that the R^n substituents could all be cis to each other an the η^3-butadienyl unit. Therefore in the case where C͡N is 8-mq the first intermediate could be (v) from which the nitrogen atom could be recoordi-

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(30) Perumaredi, J. R. *Coord. Chem. Rev.* **1969**, *4*, 73.

(31) Burdett, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 580.

(32) In the case of palladated 2-benzylpyridine compounds[25] it has been possible to isolate such cationic heterocycle associated with I^-.

(33) Taylor, S. H.; Maitlis, P. M. *J. Am. Chem. Soc.* **1978**, *100*, 4700.

nated to Pd cis to the σ-bonded carbon atom after having displaced the C=C bond that is π-bonded to Pd. The reductive elimination of Pd can then occur leading to a cationic heterocyclic compound. This later can be in thermal equilibrium with a cyclobutene-containing compound.[34] According to Woodward-Hoffman rules this should have a trans ring juncture. This compound could be easily ionized to a stable cyclobutenyl cation which would be resonance-stabilized by three of the phenyl groups. Reclosure of the heterocyclic ring would then lead to compounds **9** which do contain the more stable cyclobutene unit with a cis ring juncture.[35]

Conclusion

The main conclusions that can be inferred from this study of the insertion reactions of alkynes into the Pd-C bond of cyclopalladated amines are that these reactions can actually be controlled by the nature of the other substituents on the metal center.

For such compounds containing chloride, it is possible to isolate, in a stepwise fashion, thermally stable complexes in which one or two alkynes have been inserted into the Pd-C bonds of the starting complexes. The products in which only one alkyne is inserted into the Pd-C bond are formed with high regioselectivity.

The stability of these new organometallic expanded ring complexes is dramatically decreased by exchanging the chloride for iodide or by using the corresponding cationic complexes. These easily available modifications to the Pd center lead to high yields of heterocycles via reductive elimination of palladium(0) affording the formation of C-N bonds.

When these ligand changes are performed on the starting cyclopalladated complexes, the reactions with alkynes afford directly the heterocyclic products under the reaction conditions and, moreover, the insertion reactions are often more facile than those with the corresponding chloride-containing complexes. We have therefore discovered a convenient way to control the reactivity of both the C-Pd *and* the N→Pd bond of cyclopalladated tertiary amines.

Experimental Section

General Data. All manipulations were performed under dry oxygen-free nitrogen by using standard schlenk techniques. All solvents were dried and distilled under nitrogen prior to use. The ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 200.00 and 50.32 MHz, respectively, on a Bruker SY200 instrument Proton and carbon chemical shifts (δ, ppm, J, Hz) are positive downfield relative to external SiMe$_4$. The assignments of the carbon atoms have been elucidated by using the J-modulated spin-echo pulse sequence. Elemental analyses were carried out by the Service Central de Microanalyses du CNRS (Strabourg, France). The amount of solvent of crystallization contained in some compounds has been determined by ^{1}H NMR spectroscopy. Mass spectra were obtained with a Thomson THN 208 instrument.

Syntheses of the Starting Materials. Cyclopalladated compounds formed from *N*,*N*-dimethylbenzylamine[36] (**1**), 8-methylquinoline[37] (**2**), and *N*,*N*-dimethyl-1-naphthylamine[36] (**3**) were prepared by published methods. The iodo analogues **1***, **2***, and **3*** were obtained by metathesis of the chloro products with an excess of sodium iodide in acetone.

We advise the use of the following procedure: a twofold excess of NaI was added to a suspension of the chloride-containing cyclopalladated compound in acetone to afford a deep orange solution. After 5 min of stirring, the solvent was removed in vacuo and the iodide-containing compound was quantitatively extracted with CH$_2$Cl$_2$.

Compound 1*: ^{1}H NMR (CDCl$_3$) 3.99 and 3.96 (2s, 2 H, CH$_2$N), 2.91 and 2.88 ppm (2s, 6 H, NCH$_3$).

Compound 2*: ^{1}H NMR (CDCl$_3$) 9.29 (s (br), 1 H, H$_o$), 8.25 (dd, 1 H, H$_p$, $^3J_{H_p-H_m}$ = 7.4 Z), 3.88 (s (br), 2 H, CH$_2$).

Compound 3*: ^{1}H NMR (CDCl$_3$) 3.57 and 3.52 ppm (2s, 6 H, NCH$_3$). The presence of two singlets is due to a mixture of cis and trans isomers in a ratio of 85:15. It should be noted that **3** is present as 50:50 ratio of cis and trans isomers. Similarly, **1*** consists of a mixture of cis and trans in 74:26 ratio.

[Pd(C$_6$H$_4$CH$_2$NMe$_2$)(MeCN)$_2$]BF$_4$ (1).** To a solution of AgBF$_4$ (0.39 g, 2 mmol) in CH$_2$Cl$_2$/MeCN (15 mL/1.5 mL) was added a solution of **1** (0.55 g, 1 mmol) in CH$_2$Cl$_2$ (25 mL) giving rise instantaneously to a precipitate of AgCl. The reaction mixture was then filtered on a Celite column (l = 3 cm). The colorless filtrate was concentrated in vacuo to 2 mL, which affords by addition of pentane (30 mL) complex **1**** as a white solid (0.65 g, 80%).

Compound 1**: IR (Nujol mulls) $\nu_{C\equiv N}$ 2332, 2300 (w) cm^{-1}; ^{1}H NMR (CDCl$_3$) 3.91 (s, 2 H, CH$_2$N), 2.80 (s, 6 H, NCH$_3$), 2.47 and 2.28 ppm (2s, 6 H, CH$_3$CN). Anal. Calcd for C$_{13}$H$_{18}$BF$_4$N$_3$Pd: C, 38.12; H, 4.39; N, 10.26. Found: C, 37.89; H, 4.12; N, 10.17.

The analogous complexes **2****[38] and **3**** were prepared by the same procedure. We advise to carry on these reactions in the shortest time possible in order to obtain a better yield of the products. The total reaction time and workup should not exceed 0.5 h.

Compound 3**: IR (Nujol mulls) $\nu_{C\equiv N}$ 2310, 2290 (w) cm^{-1}; ^{1}H NMR (CDCl$_3$) 3.36 (s, 6 H, NCH$_3$), 2.55 and 2.33 ppm (2s, 6 H, CH$_3$CN). Anal. Calcd for C$_{16}$H$_{18}$BF$_4$N$_3$Pd: C, 43.13; H, 4.04; N, 9.43. Found: C, 43.04; H, 4.01; N, 9.17.

[{Pd(C(Ph)=C(CO$_2$Et)C$_6$H$_4$CH$_2$NMe$_2$)(μ-Cl)}$_2$] (4a). Ethyl 3-phenylpropiolate (0.35 g, 2 mmol) was added dropwise to a solution of [{Pd(dmba)(μ-Cl)}$_2$] (**1**) (0.55 g, 1 mmol) in dichloromethane (50 mL). The reaction mixture was stirred at room temperature for 1 h. The solvent was then removed in vacuo, and the residue was washed with pentane (3 × 10 mL). The yellow solid obtained was dissolved in CH$_2$Cl$_2$ (10 mL) and, after pentane (15 mL) has been added to it, crystallized at -20 °C affording **4a** as yellow crystals (0.53 g, 60%).

An identical procedure was used to prepare **4b** and **4c** with methyl 3-phenylpropiolate and dimethyl acetylenedicarboxylate, respectively. Elemental analyses and spectroscopic data are given in Table I.

[Pd{C(Ph)=C(CO$_2$Et)C$_6$H$_4$CH$_2$NMe$_2$}(C$_5$H$_5$N)Cl] (5a). To a solution of **4a** (0.20 g, 0.22 mmol) in dichloromethane (20 mL) at room temperature was added an excess of pyridine (0.08 g, 1 mmol) dropwise. The color of the yellow solution rapidly became lighter. The solvent was evaporated to dryness, and the residue was washed with pentane (2 × 10 mL) to remove the excess of pyridine. Compound **5a** was obtained quantitatively as a pale yellow solid which crystallized from a CH$_2$Cl$_2$/pentane solution at -20 °C.

Analogous complexes **5b** and **5c** were obtained in the same way. All analytical and spectroscopic data are reported in Table I.

[Pd{C(Ph)=C(Ph)C(Ph)=C(CO$_2$Et)C$_6$H$_4$CH$_2$NMe$_2$}Cl] (6a). An excess of diphenylacetylene (0.09 g, 0.5 mmol) was added to a solution of **4a** (0.26 g, 0.29 mmol) in dichloromethane (40 mL). After 6 h of stirring at room temperature, the orange solution was filtered to eliminate any traces of metallic palladium formed

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[34] (a) Acheson, R. M.; Paglietti, G.; Tasker, P. A. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2496. (b) Huebner, Ch. F.; Dorfman, L.; Robison, M. M.; Donoghue, E.; Pierson, W. G.; Strachan, P. *J. Org. Chem.* **1963**, *28*, 3134. (c) Kobayashi, T.; Nitta, M. *Chem. Lett.* **1983**, 1233. (d) Reinhoudt, D. N.; Verboom, W.; Visser, G. W.; Trompenaars, W. P.; Harkema, S.; van Hummel, G. J. *J. Am. Chem. Soc.* **1984**, *106*, 1341. (e) Vos, G. J. M.; Reinhoudt, D. N.; Benders, P. H., Harkema, S.; van Hummel, G. J. *J. Chem. Soc., Chem. Commun.* **1985**, 661. (f) Fried, F.; Taylor, J. B.; Westwood, R. *J. Chem. Soc., Chem. Commun.* **1971**, 1226.

[35] We thank one of the reviewers for having suggested this mechanism.

[36] Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909.

[37] Deeming, A. J.; Rothwell, I. P. *J. Organomet. Chem.* **1981**, *205*, 117.

[38] Braunstein, P.; Fischer, J.; Matt, D.; Pfeffer, M. *J. Am. Chem. Soc.* **1984**, *106*, 410.

during the reaction. The solvent was then evaporated under vacuum, and the residue was washed with pentane to remove the excess of diphenylacetylene. The orange solid thus obtained could be crystallized from a CH_2Cl_2/pentane solution at −20 °C, affording complex **6a** as orange-yellow crystals (0.37 g, 59%).

An identical procedure was used for the syntheses of compounds **6b–j**. Their analytical and spectroscopic features are given in Table II.

[Pd{C(Ph)=C(Ph)C(Ph)=C(Ph)$CH_2C_9H_6N$}Cl] (7). Diphenylacetylene (0.35 g, 1.96 mmol) was added to a suspension of [{Pd(8-mq)(μ-Cl)}$_2$] (**2**) (0.28 g, 0.5 mmol) in chlorobenzene (50 mL). After being stirred at reflux temperature for 1 h, the yellow solution was pumped dry and the remaining solid was washed with pentane (2 × 20 mL) to remove the excess of diphenylacetylene. The crude product was dissolved in a small volume of CH_2Cl_2, and pentane (30 mL) was then added to give a yellow precipitate of **7** in a pure form[11a] (0.50 g, 80%). Compound **7** could be crystallized from a CH_2Cl_2/pentane solution.

[Pd{C(Ph)=C(Ph)CH(Ph)C(Ph)=CHC_9H_6N}Cl] (8) and [{C(Ph)C(Ph)=C(Ph)C(Ph)$CH_2C_9H_6N$}$_2$]Pd_2Cl_6 (9α). A mixture of [{Pd(8-mq)(μ-Cl)}$_2$] (**2**) (0.28 g, 0.5 mmol) and diphenylacetylene (0.35 g, 1.96 mmol) in chlobenzene (50 mL) was heated at reflux for 4 h affording a dark solution, which was filtered through a Celite column (l = 4 cm) to eliminate any traces of Pd metal. The solvent was evaporated in vacuo. The crude product was washed with pentane (2 × 25 mL) to remove the unreacted diphenylacetylene. The remaining residue was dissolved in CH_2Cl_2 (25 mL); addition of pentane gave, at room temperature after 1 day, compound **9α** in very low yield (<1%) as red crystals. The mother liquor was concentrated under reduced pressure, and pentane was added giving rise to a yellow precipitate which was then further crystallized from a CH_2Cl_2/pentane solution as yellow-orange crystals **8** (0.16 g, 25%). The iodo analogue **8*** was obtained by methathesis at the chloro product with an excess of sodium iodide in acetone.

Compound 8: ^1H NMR ($CDCl_3$) 8.90 (dd, 1 H, H_o, $^3J_{H_o-H_m}$ = 4.8, $^4J_{H_o-H_p}$ = 1.6 Hz), 6.47 and 6.40 ppm (2s, 2 H, CH); ^{13}C NMR ($CDCl_3$) 95.6 (CH), 51.6 ppm (CH). Anal. Calcd for $C_{38}H_{28}ClNPd$: C, 71.26; H, 4.37; N, 2.18. Found: C, 71.50; H, 4.34; N, 2.13.

Compound 8*: ^1H NMR ($CDCl_3$) 9.37 (dd, 1 H, H_o, $^3J_{H_o-H_m}$ = 4.8, $^4J_{H_o-H_p}$ = 1.6 Hz), 6.77 and 6.65 ppm (2s, 2 H, CH). Anal. Calcd for $C_{38}H_{28}INPd$: C, 62.35; H, 3.83; N, 1.91. Found: C, 62.36; H, 3.90; N, 1.91.

Compound 9α: ^1H NMR ($CDCl_3$) 9.60 (dd, 1 H, H_o), 9.14 (dd, 1 H, H_p), 5.20 and 4.12 ppm (2d, 2 H, CH_2, $^2J_{H_A-H_B}$ = 16.3 Hz). Anal. Calcd for $C_{38.25}H_{28.5}Cl_{3.5}NPd$ (**9α** + $0.25CH_2Cl_2$): C, 62.69; H, 3.89; N, 1.91. Found: C, 62.76; H, 3.86; N, 2.06.

[{C(Ph)C(Ph)=C(Ph)C(Ph)$CH_2C_9H_6N$}$_2$]Pd_2I_6 (9β). Diphenylacetylene (0.27 g, 1.52 mmol) was reacted with [{Pd(8-mq)(μ-I)$_2$] (**2***) (0.31 g, 0.41 mmol) in chlorobenzene (50 mL) under reflux for 0.5 h. The metallic palladium formed in the reaction was filtered off (0.04 g, 63% based on Pd^0) on a Celite column (l = 4 cm). The purple solution thus obtained was pumped dry, and the residue was washed with pentane (3 × 10 mL) and dissolved in the minimum amount of CH_2Cl_2. Addition of pentane gave compound **9β** in a pure form (0.24 g, 88% based on I) which was crystallized from a CH_2Cl_2/pentane solution at room temperature affording **9β** as deep purple crystals (0.16 g, 59% based on I).

Compound 9β: ^1H NMR ($CDCl_3$) 9.23 (dd, 1 H, H_o, $^3J_{H_o-H_m}$ = 7.5 Hz), 8.65 (dd, 1 H, H_p, $^3J_{H_p-H_m}$ = 6.0, $^4J_{H_p-H_o}$ = 0.8 Hz), 8.36 (dd, 1 H, H_m), 5.14 and 4.09 ppm (2d, 2 H, CH_2, $^2J_{H_A-H_B}$ = 16.3 Hz); ^{13}C NMR ($CDCl_3$) 34.7 ppm (CH_2). Anal. Calcd for $(C_{38.5}H_{29}ClI_3NPd)_2$ (**9β** + $1CH_2Cl_2$): C, 45.50; H, 2.85; N, 1.37; Cl, 3.48. Found: C, 45.22; H, 2.66; N, 1.38; Cl, 3.48.

[C(Ph)C(Ph)=C(Ph)C(Ph)$CH_2C_9H_6N$]BF_4 (9γ). Diphenylacetylene (0.30 g, 1.68 mmol) was reacted with [Pd(8-mq)$(MeCN)_2$]BF_4 (**2****) (0.27 g, 0.65 mmol) in chlorobenzene (50 mL). The mixture was refluxed for 70 min and then filtered on a Celite column (l = 5 cm). The solvent was evaporated in vacuo, and the residue was washed with pentane (2 × 10 mL). The colorless solid obtained was dried, affording **9γ** (0.32 g, 85%) which was then chromatographed on an alumina column (l = 6 cm). Elution with CH_2Cl_2 (20 mL) eliminated some impurities (trace amounts), and further elution with acetone (40 mL) afforded a colorless solution. The acetone was pumped off, and the residue was dissolved in the minimum amount of Et_2O which at −20 °C affords **9γ** as white solid.

Compound 9γ: ^1H NMR ($CDCl_3$) 9.06 (dd, 1 H, H_o, $^3J_{H_o-H_m}$ = 7.2 Hz), 8.69 (dd, 1 H, H_p, $^3J_{H_p-H_m}$ = 6.1 Hz), 8.24 (d (br); 1 H, H_m), 4.62 and 4.06 ppm (2d, 2 H, CH_2, $^2J_{H_A-H_B}$ = 16.4 Hz). The ^1H NMR does not allow the detection of any other product. However despite of our efforts to purify it, no satisfactory elemental analyses could be obtained.

[C(CF_3)=C(CF_3)$C_{10}H_6NMe$] (10a). Hexafluorobut-2-yne (0.65 g, 4 mmol) was condensed at the liquid-nitrogen temperature into a Schlenk tube containing a solution of [{Pd(dmna)(μ-I)}$_2$] (**3***) (0.30 g, 0.37 mmol) in chlorobenzene (25 mL). The reaction mixture was heated at reflux temperature for 15 h. The solution was filtered through a Celite column (l = 5 cm), and the solution was pumped dry under vacuum giving a green solid. An extraction with pentane (3 × 10 mL) afforded an orange-red solution which, after removing the solvent, gave compound **10a** in a pure form as a red solid (0.12 g, 50%). Analytical and spectroscopic data are given in Table III.

[C(Ph)=C(Ph)$C_{10}H_6NMe$] (10b). Diphenylacetylene (0.35 g, 1.96 mmol) was added to a solution of **3*** (0.30 g, 0.37 mmol) in chlorobenzene (40 mL). The mixture was heated at reflux for 24 h, and the black solution thus obtained was filtered on a Celite column (l = 4 cm) to remove any traces of metallic palladium. The solution was taken to dryness affording a green crude product which consists of compound **10b** and the unreacted diphenylacetylene. The latter was removed by chromatography on an alumina column (l = 12 cm) using pentane (230 mL) as eluant. The pure product was then extracted with ether (40 mL) as a yellow-green solid (0.12 g, 49%) which can be crystallized, at −20 °C, from an ether/pentane solution giving fluorescent yellow crystals. **10b**: mp 201 °C; mass spectrum (CI, NH_3), m/z 334 $[(M + H)^+]$, 333 (M), 318 $[(M + H)^+ - Me]$, 241 $[(M + H)^+ - Me - Ph]$.

[C(Ph)=C(CO_2Et)$C_{10}H_6NMe$] (10c). A mixture of **3*** (0.40 g, 0.49 mmol) in chlorobenzene (45 mL) with ethyl 3-phenylpropiolate (0.35 g, 2 mmol) was refluxed for 2 h. The metallic palladium obtained was removed by filtration on a Celite column (l = 4 cm). The solvent was pumped off under vacuum, and the khaki waxy solid obtained was washed with hexane (5 mL) affording **10c** as a green solid (0.32 g, 96%) contaminated with free alkyne. Crystallization from an ether/pentane solution at −20 °C gave **10c** as fluorescent yellow-green crystals (0.13 g, 40%); mp 117 °C. The mother liquor was pumped to dryness and the residue purified by chromatography on an alumina column (l = 20 cm). Free alkyne was first extracted with pentane (500 mL). The loss of some amount of **10c** could not be prevented. The pure product was then extracted with ether (250 mL) (0.09 g, 30%) resulting in a total yield of 70%: mass spectrum (EI), m/z 329 $[(M)^+]$, 314 $[(M)^+ - Me]$, 284 $[(M)^+ - OEt]$, 252 $[(M)^+ - Ph]$. When a solution of **10c** in $CDCl_3$ is kept in the presence of air, it turns purple after 1 day. This leads to the following new ^1H NMR data: 3.82 (m, 2 H, OCH_2), 2.85 (s, (br), 3 H, NCH_3), 0.79 ppm (td, 3 H, CH_3). This latter compound could not be characterized.

[C(CO_2Me)=C(CO_2Me)$C_{10}H_6NMe$] (10d). Dimethyl acetylenedicarboxylate (0.20 g, 1.4 mmol) was added to a solution of **3*** (0.30 g, 0.37 mmol) in chlorobenzene (40 mL). After the solution was stirred at reflux temperature for 70 min, the color became dark green. The solution was filtered through a Celite column, and the solvent was pumped off in vacuo; the green residue then obtained was washed with hexane (5 mL). Extraction with a mixture of CH_2Cl_2/hexane (2 mL/15 mL) afforded an orange solution which after removal of the solvent gave **10d** as an orange solid (0.22 g, 50%). When the CH_2Cl_2/hexane solution was concentrated and cooled at −20 °C, compound **10d** was obtained as bright orange crystals (0.05 g, 23%); mp 92 °C; mass spectrum (CI, CH_4), m/z 297 $[(M)^+]$, 282 $[(M)^+ - Me]$, 266 $[(M)^+ - OMe]$.

[{C(Ph)=C(CO_2Et)C_6H_4CH=NMe}$_2$]Pd_2I_6 (11) and [C-

$(Ph){=}C(CO_2Et)C_6H_4CH{=}N]$ (12). A solution of **4a*** (0.45 g, 0.42 mmol) in chlorobenzene (50 mL) was refluxed for 3 h. The black solution thus obtained was filtered on a Celite column (l = 4 cm). The solvent was removed from the purple solution by evaporation under reduced pressure. Pentane (30 mL) was then added to the crude product, and the mixture was stirred for 3 h. The suspension was filtered to separate the dark solid from the yellow solution. The solid was then crystallized at room temperature from a CH_2Cl_2/pentane solution to give compound **11** as purple crystals (0.01 g, 14% based on dmba). The pentane of the yellow solution was pumped off in vacuo leading to an organic oil, **12** (0.10 g, 60% based on dmba).

Compound 11: IR (KBr) $\nu_{C=O}$ 1725 (s) cm^{-1}; ^{1}H NMR (CD_2Cl_2) 10.45 (s, 1 H, CH=N), 4.50 (s, 3 H, NCH_3), 4.16 (q, 2 H, OCH_2), 0.93 ppm (t, 3 H, CH_3); mass spectrum (CI, CH_4), m/z 292 [(M)$^+$], 277 [(M)$^+$ - (Me)], 248 [(M)$^+$ - Me - Et], 232 [(M)$^+$ - Me - OEt], 204 [(M) - Me - CO_2Et]. Anal. Calcd for $C_{19}H_{18}I_3NO_2Pd$: C, 29.26; H, 2.31; N, 1.79. Found: C, 29.33; H, 2.28; N, 1.76.

Compound 12: IR (film) $\nu_{C=O}$ 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) 9.35 (s, 1 H, CH=N), 4.22 (q, 2 H, OCH_2), 1.02 ppm (t, 3 H, CH_3); mass spectrum (CI, CH_4), m/z 278 [(M + 1)$^+$], 277 [(M)$^+$].

$[C(Ph)C(Ph){=}C(Ph)C(Ph)C_6H_4CH_2NMe_2]BF_4$ (13). To a chlorobenzene (50 mL) solution of $[Pd(dmba)(MeCN)_2]BF_4$ (**1****) (0.25 g, 0.61 mmol) was added diphenylacetylene (0.25 g, 1.40 mmol), and the mixture was refluxed for 2.5 h. The metallic palladium thus formed was filtered off on a Celite column (l = 5 cm). The chlorobenzene was removed in vacuo, and the remaining orange residue was washed with pentane (2 × 10 mL), redissolved in the minimum amount of CH_2Cl_2, and precipitated by addition of pentane (25 mL) affording a yellow-orange solid (**13**) in quantitative yield. Its ^{1}H NMR spectrum did not show any other product than **13**. This product was purified by crystallization from CH_2Cl_2/pentane solution at -20 °C giving compound **13** as bright yellow crystals (0.13 g, 37.5%), mp 204 °C.

Compound 13: IR (KBr) ν_{BF} 1070 (s, br) cm^{-1}; ^{1}H NMR ($CDCl_3$) 5.83 (d, 1 H, aromatic proton, $^3J_{H-H}$ = 7.8 Hz), 4.21 and 3.88 (2d, 2 H, CH_2N, $^2J_{H_A-H_B}$ = 13.6 Hz), 2.70 and 1.74 ppm (2s (br), 6 H, NCH_3); mass spectrum (EI), m/z 489 [(M - 1)$^+$], 474 [(M - 1)$^+$ - Me], 412 [(M - 1)$^+$ - Ph]. Anal. Calcd for $C_{37}H_{32}BF_4N$: C, 76.97; H, 5.54; N, 2.43. Found: C, 76.73; H, 5.65; N, 2.34.

$[C(CO_2^-)C(Ph){=}C(Ph)C(CO_2Et)C_6H_4CH_2N^+Me_2]$ (14). Ethyl 3-phenylpropiolate (0.26 g, 1.49 mmol) was added to a solution of $[Pd(dmba)(MeCN)_2]BF_4$ (**1****) (0.25 g, 0.61 mmol) in chlorobenzene (40 mL). The mixture was heated at reflux for 70 min affording a black solution. The metallic palladium thus formed was removed by filtration on a Celite column (l = 4 cm), and the solvent was evaporated to dryness in vacuo. The resulting solid was purified by chromatography on an alumina column (l = 6 cm) using CH_2Cl_2 as eluant. The orange solution obtained was pumped dry affording **14** as an orange waxy solid which could not be crystallized.

Compound 14: IR (KBr) $\nu_{C=O}$ 1720 (s) (CO_2R), 1615 (m) (CO_2^-) cm^{-1}; ^{1}H NMR (CD_2Cl_2) 7.70–6.94 (m, 14 H, aromatic protons), 3.79 (q, 2 H, OCH_2), 3.22 and 3.33 (2d, 2 H, CH_2N, $^2J_{H_A-H_B}$ = 13.8 Hz), 2.16 (s, 6 H, NCH_3), 0.77 ppm (t, 3 H, CH_3); mass spectrum (EI), m/z 453 [(M)$^+$ (molecular pic confirmed by its CI spectrum)], 424 [(M)$^+$ - Et], 408 [(M)$^+$ - OEt].

$[C(CO_2^-)C(Ph){=}C(Ph)C(CO_2Et)CH_2C_9H_6N^+]$ (15). Starting from $[Pd(8\text{-mq})(MeCN)_2]BF_4$ (**2****) (0.21 g, 0.5 mmol) and ethyl 3-phenylpropiolate (0.21 g, 1.2 mmol) in chlorobenzene (50 mL) and with a procedure identical with that used for **14**, compound **15** was obtained. The presence of some impurities could not be prevented, and good analytical data could not be obtained.

Compound 15: IR (KBr) $\nu_{C=O}$ 1715 (s) (CO_2R), 1615 (m) (CO_2^-) cm^{-1}; ^{1}H NMR (CD_2Cl_2) 8.80 (dd, 1 H, H_o, $^3J_{H_o-H_m}$ = 4.2, $^4J_{H_o-H_p}$ = 1.8 Hz), 8.14 (dd, 1 H, H_p, $^3J_{H_p-H_m}$ = 8.3 Hz), 7.70–7.17 (m, 14 H, aromatic protons), 4.38 (s (br), 2 H, CH_2), 3.79 (q, 2 H, OCH_2), 0.80 ppm (t, 3 H, CH_3).

$[C(Ph){=}C(CO_2Et)C_6H_4CH_2NMe_2]BF_4$ (16). Heating compound **4a**** (0.65 g, 1.11 mmol) in refluxing chlorobenzene (40 mL) for 0.75 h leads to the quantitative formation of Pd metal. The mixture was filtered on a Celite column (l = 4 cm), and then the solvent was evaporated under vacuum. The residue thus obtained was purified by chromatography on an alumina column (l = 7 cm). The CH_2Cl_2 (50 mL) was first used as eluant in order to eliminate impurities, and then extraction with acetone (35 mL) affords, after the solvent was removed, compound **16** as a colorless solid (0.18 g, 41%).

Table IV. A Summary of Crystal Data and Intensity Collection of 9α and 11

	9α	11
formula	$C_{38}H_{28}Cl_3NPd$	$C_{19}H_{18}I_3NO_2Pd$
cryst system	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$
a/Å	10.407 (4)	13.364 (8)
b/Å	16.354 (3)	12.316 (4)
c/Å	9.992 (5)	14.645 (9)
α/deg	92.09 (2)	90.0
β/deg	109.23 (5)	105.45 (3)
γ/deg	80.50 (2)	90.0
U/Å^3	1583.3	2323.2
M_r	711	779
Z	2	4
cryst dimens/mm	0.35 × 0.30 × 0.26	0.45 × 0.42 × 0.13
λ(Mo Kα)/Å	0.71073	0.71073
μ/cm^{-1}	8.60	47.5
F(000)	720	1440
scan range/deg	100 + 0.35 tan θ	1.00 + 0.35 tan θ
θ limits/deg	1–25	1–25
reflctns, total	5906	4473
reflctns, used	3734 ($I > \sigma(I)$)	2700 ($I > 3\sigma(I)$)
R factor, %	3.5	6.4
R_w factor, %	4.7	8.4
std error in an observn of unit weight, e	1.73	2.70

Compound 16: IR (KBr) $\nu_{C=O}$ 1725 (s) (CO_2R), ν_{BF} = 1060 (s, br) cm^{-1}; ^{1}H NMR ($CDCl_3$) 5.06 (s, 2 H, CH_2N), 3.99 (q, 2 H, OCH_2), 3.26 (s, 6 H, NCH_3), 0.85 ppm (t, 3 H, CH_3); mass spectrum (CI, CH_4), m/z 309 [(M + 1)$^+$], 294 [(M + 1)$^+$ - Me], 293 [(M + 1)$^+$ - H - Me], 264 [(M + 1)$^+$ - H - Me - Et], 248 [(M + 1)$^+$ - H - Me - OEt].

$[C(Ph){=}C(Ph)C_{10}H_6NMe_2]BF_4$ (17a). Diphenylacetylene (0.25 g, 1.4 mmol) was added to a solution of $[Pd(dmna)(MeCN)_2]BF_4$ (**3****) (0.23 g, 0.51 mmol) in chlorobenzene (60 mL). The reaction mixture was refluxed for 1 h and filtered on a Celite column (l = 5 cm) to remove metallic palladium. The dark red solution thus obtained was pumped dry under vacuum affording a solid that was washed with pentane (2 × 10 mL). The product **17a** was formed together with **3** in a ratio of 3:1 (NMR data). From a CH_2Cl_2/pentane solution compound **17a** crystallized at room temperature as dark purple crystals (0.04 g, 18%).

Compound 17a. IR (KBr) ν_{BF} = 1050 (s, br) cm^{-1}; ^{1}H NMR (CD_3CN) 6.92 (d, 1 H, H^4, $^3J_{H4-H5}$ = 6.4 Hz), 3.76 ppm (s, 6 H, NCH_3); mass spectrum (EI), m/z 347 [(M - 1)$^+$], 333 [(M)$^+$ - Me], 318 [(M)$^+$ - 2Me]. Anal. Calcd for $C_{26.25}H_{22.5}BCl_{0.5}F_4N$ (**17a** + $0.25CH_2Cl_2$): C, 69.07; H, 4.93; N, 3.07. Found: C, 68.66; H, 4.93; N, 2.94.

$[C(Ph){=}C(CO_2Et)C_{10}H_6NMe_2]BF_4$ (17b). Ethyl 3-phenylpropiolate (0.15 g, 0.86 mmol) was added to a solution of **3**** (0.20 g, 0.46 mmol) in chlorobenzene (50 mL). The reaction mixture was heated at reflux for 2 h, and then metallic palladium was removed by filtration on a Celite column (l = 4 cm) giving a dark green solution. The solvent was evaporated in vacuo, and the residue thus obtained was washed with pentane (2 × 10 mL) and then with ether (15 mL) to remove any traces of **10c** formed upon the reaction. The remaining green solid consisted of compound **17b** contaminated with $[\{Pd(dmna)(\mu\text{-}Cl)\}_2]$ (**3**); thus **17b** could not be obtained in a pure form.

Compound 17b: IR (KBr) $\nu_{C=O}$ 1720 (s), ν_{BF} 1050 (s, br) cm^{-1}; ^{1}H NMR ($CDCl_3$) 4.02 (q, 2 H, OCH_2), 3.89 (s, 6 H, N-CH_3), 0.91 ppm (t, 3 H, CH_3).

X-ray Diffraction. Intensities were measured on an Enraf-Nonius CAD-4 diffractometer. The crystal parameters and a summary of data collection and structure refinement are given in Table IV. No intensity decay was observed during the data collection period. No absorption corrections were applied.

The structures were solved by the Enraf-Nonius SDP package on a PDP 11-60 computer.[39] The atomic positions of the independent 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 9α, 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.

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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; 9α, 109802-53-1; 9β, 109802-41-7; 9γ, 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 9α and 11 (15 pages); listings of observed and calculated structure factors for 9α 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.

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