Reactivity of Cyclopalladated Compounds. Part 18.[1] Compared Reactivity of the Pd–C Bonds of Two Closely Related Six-membered Palladocyclic Rings with Substituted Alkynes. *X*-Ray and Molecular Structures of $[Pd\{C(Ph)=C(R)C(Ph)=C(R)(o\text{-}C_6H_4N=CMeNHPh)\}Cl]$ ($R = CO_2Et$) and $[Pd\{C(R)[C(CO_2Me)C(R)=C(R)C(R)=C(R)][o\text{-}C_6H_4N=CMe(OH)]\}Cl]$ ($R = CO_2Me$)†

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The reactions between alkynes and the chloride-bridged cyclopalladated dimers derived from orthopalladation of acetanilide, $[\{Pd(o\text{-}C_6H_4NHCMe=O)\}_2(\mu\text{-}Cl)_2]$ (**1**), and amidine, $[\{Pd(o\text{-}C_6H_4NHCMe=NPh)\}_2(\mu\text{-}Cl)_2]$ (**2**), afforded organometallic products in which one, two, or three alkynes had been inserted into the Pd–C bonds of (**1**) and (**2**), the ratio of alkyne:palladium in the final products being independent of the stoicheiometry of the reaction. Compound (**1**) gave with hexafluorobut-2-yne the mono-inserted product $[\{Pd[C(CF_3)=C(CF_3)(o\text{-}C_6H_4NHCMe=O)](\mu\text{-}Cl)\}_2]$. With diphenylacetylene it gave an unstable product (**7**) in which two alkynes had been added per palladium atom forming with the acetanilide unit a spirocyclic ligand η^3-bonded to the palladium centre. Compound (**7**) decomposed on heating to afford quantitatively the pentasubstituted naphthalene derivative $C_{10}H_3Ph_4(NHCMe=O)$. Compound (**2**) reacted with diphenylacetylene and ethyl 3-phenylpropionate to give the di-inserted products $[Pd\{C(Ph)=C(R)C(Ph)=C(R)(o\text{-}C_6H_4N=CMeNHPh)\}Cl]$ (**11**, R = Ph; **12**, R = CO_2Et). The structure of (**12**) was ascertained by an *X*-ray structure determination, which confirmed the regioselectivity of the insertion reaction and that (**12**) is an eight-membered palladocyclic ring through the co-ordination to the metal of the nitrogen atom immediately adjacent to the phenyl ring. Triple insertion of alkynes was observed when reacting (**1**) and (**2**) with dimethyl acetylenedicarboxylate affording $[Pd\{C(CO_2Me)[C(CO_2Me)C(CO_2Me)=C(CO_2Me)C(CO_2Me)=C(CO_2Me)(o\text{-}C_6H_4N=CMeYH)]\}Cl]$ (**9**, Y = O; **13**, Y = NPh). The structure of (**9**) has been confirmed by an *X*-Ray diffraction study. A related triple insertion occured when treating (**1**) with but-2-yne affording a thermally unstable intermediate; its depalladation led to *trans*-*o*-$C_6H_4(NHCMe=O)CH=CH(C_5Me_5)$.

Among the various reactions that have been reported to occur with the Pd–C bonds of cyclopalladated complexes, the insertion of alkynes has recently been shown to be very attractive, either leading to new organometallic compounds through ring enlargement,[2] or selectively affording organic heterocycles *via* one-pot synthesis of C–C and C–N[3] or C–S[4] bonds. The different reaction paths that have been described so far depend on many factors and obviously the nature of the three-electron donor chelates is of basic importance in determining the type of reaction that is likely to occur with alkynes.

The main objective of this study is to describe the chemistry of two closely related cyclopalladated compounds, $[\{Pd(o\text{-}C_6H_4NHCMe=O)\}_2(\mu\text{-}Cl)_2]$ (**1**) and $[\{Pd(o\text{-}C_6H_4NHCMe=NPh)\}_2(\mu\text{-}Cl)_2]$ (**2**), obtained with acetanilide and amidine respectively.[5] Indeed, these two compounds are interesting in several respects. (*i*) They differ only in the nature of the donor atom, *i.e.* oxygen *vs.* a N–Ph unit, and thus the study of their reactivity should allow us to compare the role of the heteroatom upon the course of the insertion of alkynes into the Pd–C bonds. (*ii*) The metallocyclic units of both complexes contain six atoms, a feature that is relatively rare for these types of complexes. A related compound containing cyclopalladated 2-benzylpyridine[2c,d] displayed an unusually high and rich reactivity when compared with the more common compounds in which the palladium is part of a five-membered ring. (*iii*) These starting materials contain another heteroatom (*i.e.* a nitrogen atom) within the metallocyclic unit, for which it could be reasonably expected to play an important role in the course of the reaction.

In this paper we describe the reaction of (**1**) and (**2**) with a

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† Chloro(2,4-diethoxycarbonyl-1,3-diphenyl-4-{*o*-[1-(phenylamino)-ethylideneamino]phenyl}buta-1,3-dien-1-yl-C^1,$C^{3,4}$,*N*)palladium(II) and [(carboxymethyl[pentakis(methoxycarbonyl)cyclopenta-2,4-dien-1-yl]{*o*-[(1-hydroxy)ethylideneamino]phenyl})methyl-*N*,*O*]chloropalladium(II) respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

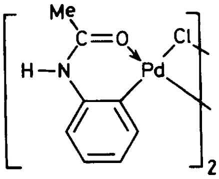
variety of substituted alkynes and show that these reactions: (*a*) lead to the formation of organometallic or organic products whose structures are very different from those already described,[2] and (*b*) result, in most cases, in an improved reactivity of the Pd–C bond compared with that of the other cyclopalladated compounds studied so far.[3]

Results and Discussion

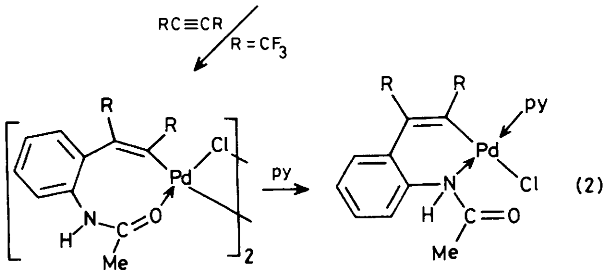
The synthesis of compounds (**1**) and (**2**) was first described using PdCl$_2$ as the metallating agent.[5] However, recently it was shown that palladium acetate must be used to achieve the cyclopalladation of acetanilide.[6] Whereas the reactions of (**1**) with electrophiles or olefins has been investigated,[6,7] no in-depth studies have so far been reported for the cyclopalladated amidine complex (**2**). Moreover, several points concerning the structure of this latter compound and its reaction with pyridine (py) remain unclear. Cameron and Kilner[5] assigned a polymeric structure to the cyclopalladated amidine compound; on reaction with pyridine it was thought to afford the chloride-bridged dimer (**2**) and the white monomer [Pd(*o*-C$_6$H$_4$NHCMe=NPh)Cl(py)]. We found that treating (**2**) with an excess of pyridine immediately afforded a colourless solution which led to precipitation of compound (**3**) as a white powder, which was then totally insoluble in any common organic solvents. We believe that this latter compound cannot be the monomeric pyridine adduct for the following reasons. (*i*) The reaction between (**2**) and one equivalent of Bu^{t}NC afforded the monomeric compound [Pd(*o*-C$_6$H$_4$NHCMe=NPh)(Bu^{t}NC)Cl] (**4**) which is soluble in common organic solvents. Compound (**3**), on the other hand, is insoluble to such an extent that we were unable to record a ^{1}H n.m.r. spectrum. (*ii*) The i.r. spectrum of (**3**) showed a strong and broad absorption at *ca.* 3 000 cm^{-1} which is good evidence for the presence of a pyridinium proton. (*iii*) Compound (**2**) could be totally regenerated by treating (**3**) with HCl in water.

We conclude from this set of experiments that compound (**2**) is indeed a chloride-bridged dimer and not a polymer as stated earlier.[5] The reaction of (**2**) with excess pyridine led to an initial dissolution of the product as a probable consequence of a bridge splitting reaction. This was then followed by slow deprotonation of the nitrogen atom of the amidine function affording a pyridinium cation associated with an anionic organo-palladium species. Because of its marked insolubility we believe that it might have a polymeric structure [see equation (1)] in which a Pd atom is linked to two different amidine ligands *via* a three-electron donor-bonded amidine group,[8] and also *via* the *ortho* carbon atom of a phenyl ring.

Reactions of Cyclopalladated Acetanilide with Alkynes.—The cyclopalladated complex (**1**) reacts, in dichloromethane at room temperature, with an excess of hexafluorobut-2-yne to afford compound (**5**) [equation (2)]. Elemental analyses are consistent with the addition of one alkyne unit per palladium centre. The co-ordination of an amide function to a metal centre *via* its oxygen atom is usually detected by the presence of two absorptions in the i.r. spectrum in the range 1 650—1 550 cm^{-1}.[9] Thus, the occurrence of two bands at 1 608 and 1 590 cm^{-1} in the i.r. spectrum of (**5**) strongly suggests that the oxygen atom of the amide function is indeed co-ordinated to the palladium atom.



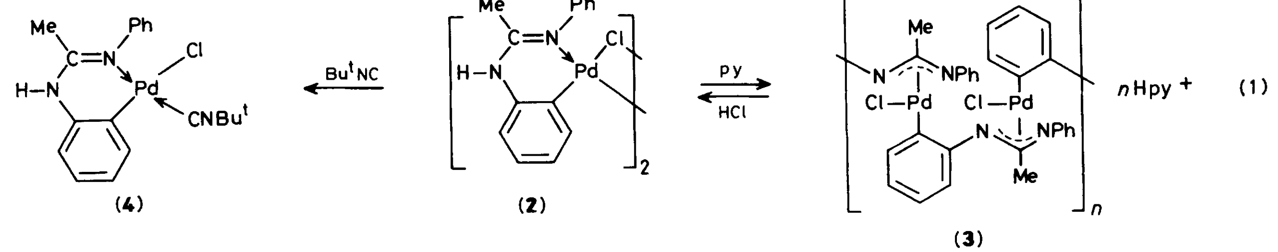
(**1**)



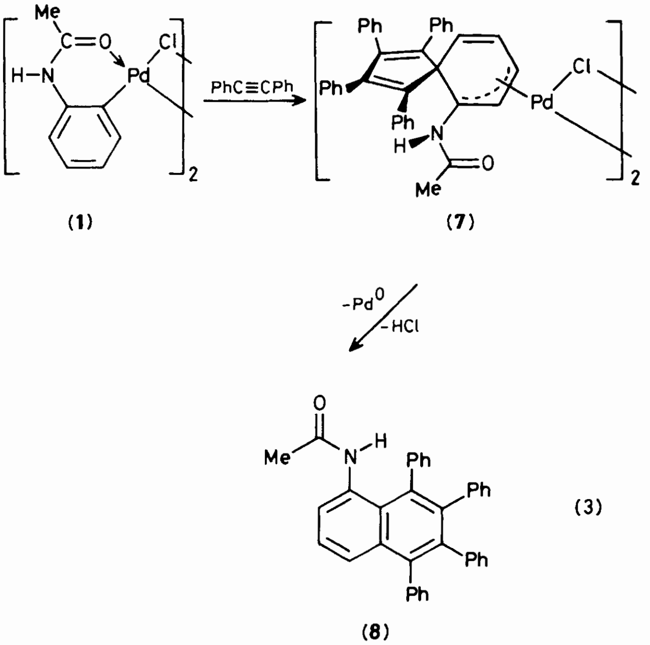
(**5**) (**6**)

Cleavage of the chloride bridges in the dipalladium complex [{Pd[C(CF$_3$)=C(CF$_3$)(*o*-C$_6$H$_4$NHCMe=O)](μ-Cl)}$_2$] (**5**) by pyridine led to the monomeric compound (**6**). Its i.r. spectrum shows an intense absorption at 1 698 cm^{-1} for the CO group of the amide unit. This value, which is close to that of the free amide, indicates, in this case, that the oxygen atom is probably not co-ordinated to the palladium atom. The ^{1}H n.m.r. spectrum of (**5**) shows the presence of two sets of signals, which can be easily explained by the fact that (**5**) exists as *cis* and *trans* isomers in a 1 : 1 ratio; the ^{1}H n.m.r. of (**6**) also shows the presence of two isomers (in a 1 : 4 ratio) in which the pyridine is co-ordinated to the palladium either *trans* to the carbon or *trans* to the nitrogen atom, respectively. This result is in contrast to that previously observed in most cases for the cleavage of chloride bridges by pyridine in related compounds. In most of the cases we have studied so far[2d] this led to the formation of only one isomer with the pyridine being *trans* to the nitrogen of the metallocyclic unit. However, a result analogous to that observed here has already been described.[2a]

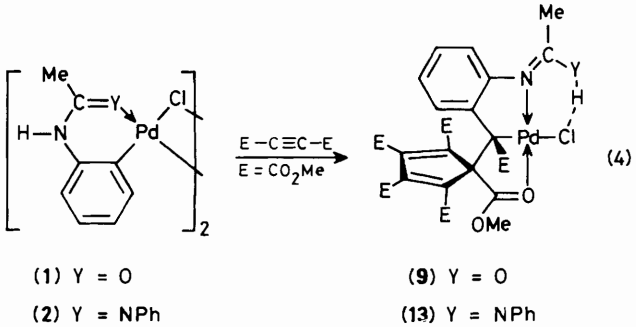
When compound (**1**) was treated with an excess of diphenylacetylene, in dichloromethane at room temperature, it afforded good yields of compound (**7**) which proved to be rather unstable in solution at room temperature. Elemental analyses indicated that two alkyne units had been added per palladium atom. Despite all our efforts no interpretable ^{1}H n.m.r. spectrum could be obtained for this compound even at −80 °C in CD$_2$Cl$_2$. However, its ^{13}C-{^{1}H} n.m.r. spectrum showed several high-



(**4**) (**2**) (**3**)



(1) (7) (3) (8)



(4)

(1) Y = O (9) Y = O

(2) Y = NPh (13) Y = NPh

field shifted aromatic carbon atoms. This feature might be rationalised if we assume that (**7**) contains a spiro ligand which is η^3-bonded to Pd *via* a hexadienyl unit as shown in equation (3). Nevertheless, this statement is far from being firmly established because of the lack of reasonable ^{1}H n.m.r. data. Our hypothesis is, however, not unlikely since a similar result has been recently reported for a related six-membered palladocyclic ring in which the nitrogen atom of a pyridine unit was strongly co-ordinated to the palladium centre.[2c] In the case of compound (**7**) the lower co-ordinating ability of the oxygen atom of the amide function [ν(C=O) 1 700 cm^{-1}] might well explain its marked instability.

When compound (**7**) was allowed to completely decompose in solution (after 0.3 h in refluxing PhCl solution) reasonable yields (after recrystallisation) of an organic product (**8**) were obtained which was characterised by analytical and spectroscopic data. We propose that it is a neutral pentasubstituted naphalthene with an amido group on one of the peri positions. An analogous cationic unit has been obtained very recently using a cationic cyclopallated complex of *NN*-dimethylbenzylamine which was treated with hex-3-yne.[3c] In that case, however, the proton that was evolved during the rearrangement of the organometallic moiety (which, incidentally, was also believed to be a spirane derivative) was found on the tertiary nitrogen atom. This feature was perhaps not observed in this case because of the lower basicity of an amido unit compared with that of a tertiary amine.

These results proved that the Pd–C bond of (**1**) has a markedly increased reactivity as compared to related neutral cyclopalladated complexes, since in the present study depalladation could be achieved without further activating the complex by changing the other ligands in the Pd co-ordination sphere. This feature was also demonstrated by studying the reaction between (**1**) and an excess of dimethyl acetylenedicarboxylate (dmad). It afforded a quantitative yield of compound (**9**) [equation (4)].

The analytical data indicated that the formula of (**9**) was derived from that of (**1**) with the inclusion of three dmad units. A remarkable feature of this reaction is that it is independent of the stoicheiometry used: even when a Pd:dmad ratio greater than 1:3 was used, compound (**9**) was obtained together with the corresponding unreacted (**1**). An *X*-ray diffraction study has been carried out on (**9**) to determine unambigously the geometry of this molecule. An ORTEP view is shown in Figure 1. Selected distances and angles are given in Table 1.

The reaction between (**1**) and three equivalents of dmad resulted in the formation of a new terdendate ligand which is linked to palladium *via* one σ-bonded carbon atom [C(21)], an oxygen atom of a methoxycarbonyl group [O(221)], and the nitrogen atom of an amido unit, the geometry around the palladium atom being that of a distorted square plane. Interestingly, the insertion of the alkynes into the σ Pd–C bond of (**1**) was accompanied by the migration of the H atom from N(1) to O(11), thus forming a hydrogen bond with the Cl atom [O(11)–H 0.86(5) Å, Cl···H 2.12(5) Å, O(11)–H···Cl 172(5)°]. The three alkyne units form a pentakis(methoxycarbonyl)cyclopentadienyl moiety, also substituted at C(22) by a $\{C(CO_2Me)[o\text{-}C_6H_4N{=}C(Me)(OH)\}Pd$ group. One oxygen atom of the CO_2Me group at C(22) forms a co-ordination bond to the palladium centre, thus defining another five-membered palladocyclic ring.

This type of arrangement of three dmad units is very similar to that found earlier by Maitlis and co-workers[10] when studying the oligomerisation of dmad with palladium chloride. In marked contrast with our results however, these authors found that the trimerized alkyne unit formed a six-membered palladocyclic ring by using the co-ordination ability of a different ester carbonyl group, *e.g.* the CO_2Me function that is immediately adjacent to the sp^3 atom of the cyclopentadienyl unit.

The insertion of three alkyne units into the Pd–C bonds of cyclopalladated complexes seems to be a common feature of these compounds as recently two independent such reactions have been reported for cationic cyclopalladated complexes which were thought to be activated.[2d,3c] Moreover, several quite recent related results have been observed in our laboratory for cyclopalladated complexes containing either nitrogen or sulphur as the donor atoms.[11]

The great reactivity of the Pd–C bond of (**1**) was further demonstrated by treating it with an excess of but-2-yne in dichloromethane. This afforded rapidly an orange organometallic intermediate which proved to be rather unstable in solution so that it was impossible to obtain a reasonable ^{1}H n.m.r. spectrum (even at low temperature). However the organic product (**10**) (which was cleanly and quantitatively obtained at 60 °C in chlorobenzene as white crystals) that resulted from depalladation of this organometallic compound, was shown by analytical data to consist of an *ortho*-substituted acetanilide moiety coupled to three but-2-yne units. The ^{1}H n.m.r. and mass spectra allow us to propose for (**10**) the structure depicted in equation (5). The rationalisation for its formulation is quite similar to that invoked earlier for the synthesis of *trans*-β-(pentamethylcyclopentadienyl)styrene obtained *via* the thermal decomposition of the organometallic product formed from the reaction of 'PdPhCl' and but-2-yne.[12]

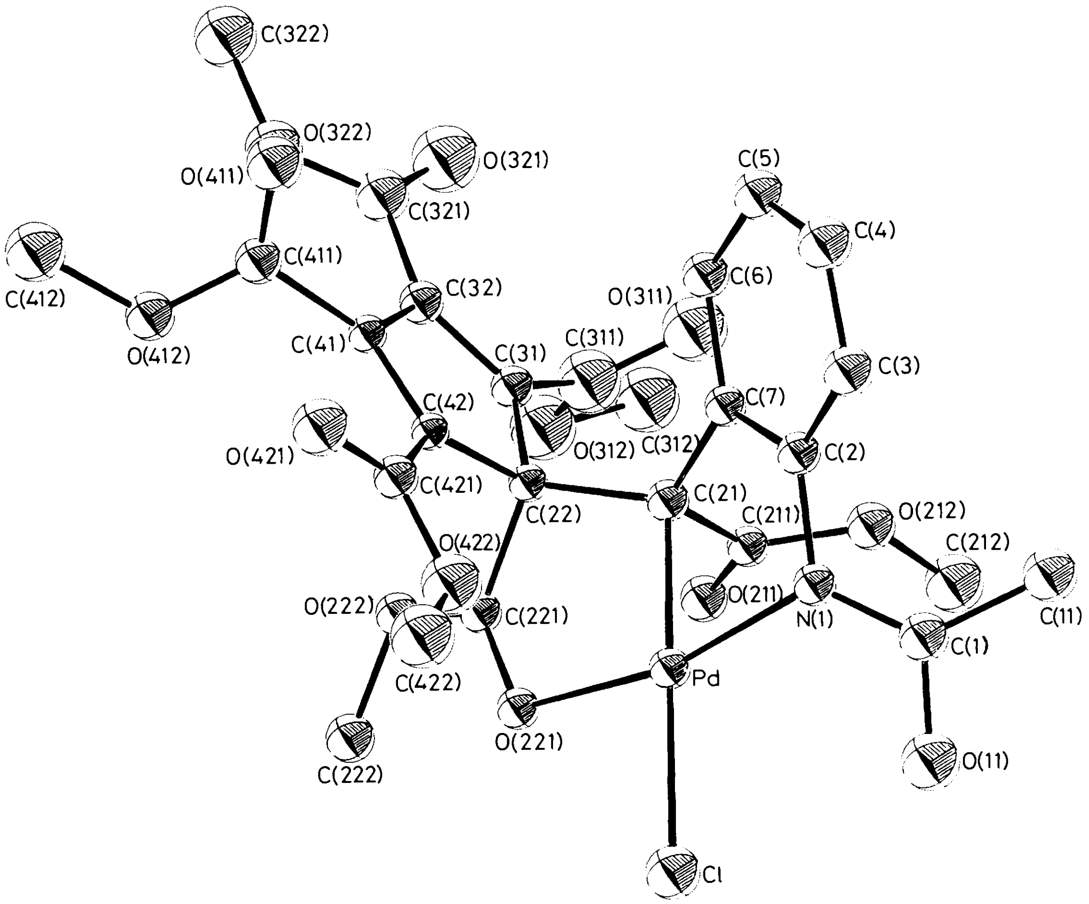
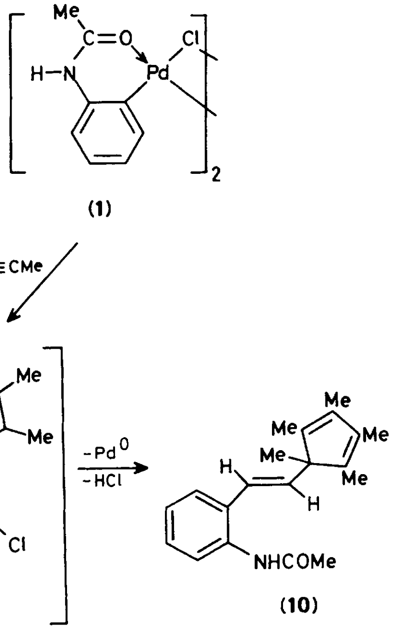


Figure 1. ORTEP view of compound (**9**). Ellipsoids represent 30% probability

Table 1. Selected interatomic distances (Å) and bond angles (°) for compound (**9**)

Pd-Cl	2.3890(7)	C(22)-C(221)	1.530(4)
Pd-N(1)	2.031(2)	C(22)-C(31)	1.532(4)
Pd-C(21)	2.026(3)	C(22)-C(42)	1.538(3)
Pd-O(221)	2.096(2)	C(221)-O(221)	1.227(3)
N(1)-C(1)	1.288(4)	C(31)-C(32)	1.340(4)
N(1)-C(2)	1.435(4)	C(32)-C(41)	1.461(4)
C(7)-C(21)	1.493(4)	C(41)-C(42)	1.338(4)
C(21)-C(22)	1.562(3)		
N(1)-Pd-Cl	100.02(7)	C(22)-C(21)-C(211)	108.9(2)
C(21)-Pd-Cl	176.14(8)	C(221)-C(22)-C(21)	105.1(2)
C(21)-Pd-N(1)	82.4(1)	C(31)-C(22)-C(21)	114.5(2)
O(221)-Pd-Cl	95.17(5)	C(42)-C(22)-C(21)	117.8(2)
O(221)-Pd-N(1)	164.81(9)	C(42)-C(22)-C(31)	100.9(2)
O(221)-Pd-C(21)	82.48(8)	C(32)-C(31)-C(22)	110.0(2)
C(2)-N(1)-C(1)	122.2(3)	C(41)-C(32)-C(31)	109.5(2)
O(11)-C(1)-N(1)	120.0(3)	C(42)-C(41)-C(32)	110.0(2)
C(22)-C(21)-C(7)	118.1(2)	C(41)-C(42)-C(22)	109.5(2)



(5)

Reactions of Cyclopalladated Amidine with Alkynes.—The sparingly soluble complex (**2**) does not give a clear reaction with hexafluorobut-2-yne. After 48 h in dichloromethane only traces of a yellow compound were isolated. Moreover, since this reaction seemed not to be reproducible, we decided not to investigate it any further. On the other hand, heating an excess of diphenylacetylene and (**2**) in chlorobenzene at reflux afforded an orange-brown solution from which yellow-orange crystals were obtained in high yield. The product was formulated as a bis-insertion complex (**11**) [equation (6)]. In contrast to (**7**),

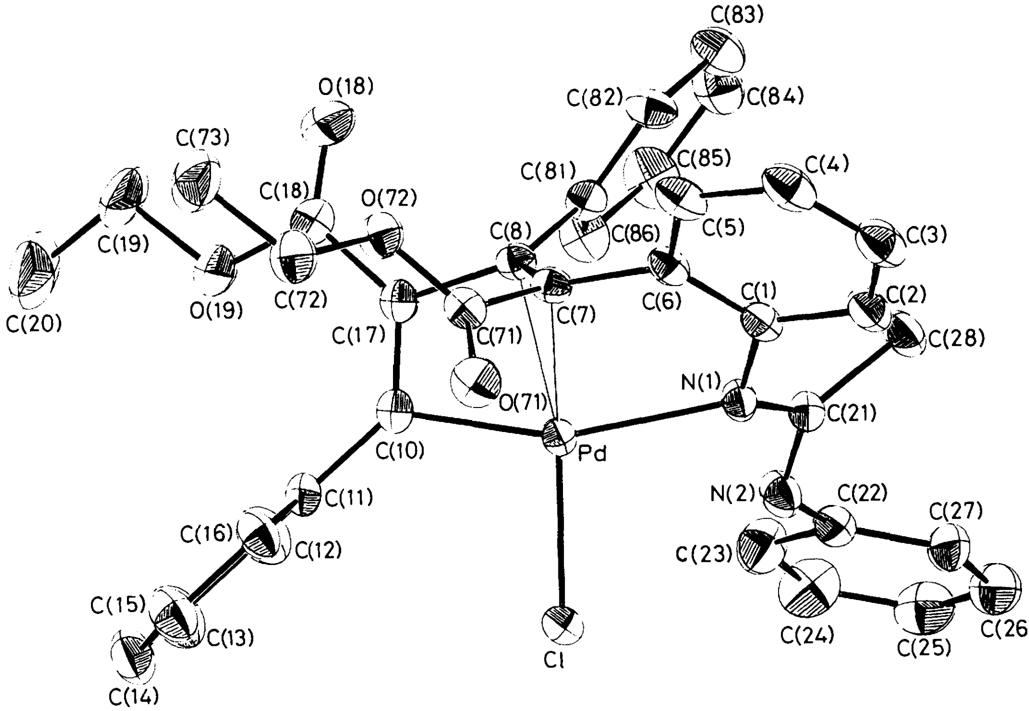
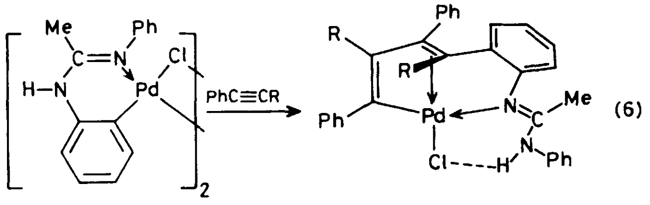


Figure 2. ORTEP view of compound (**12**). Ellipsoids represent 30% probability



(**2**) (**11**) R = Ph

(**12**) R = CO_2Et

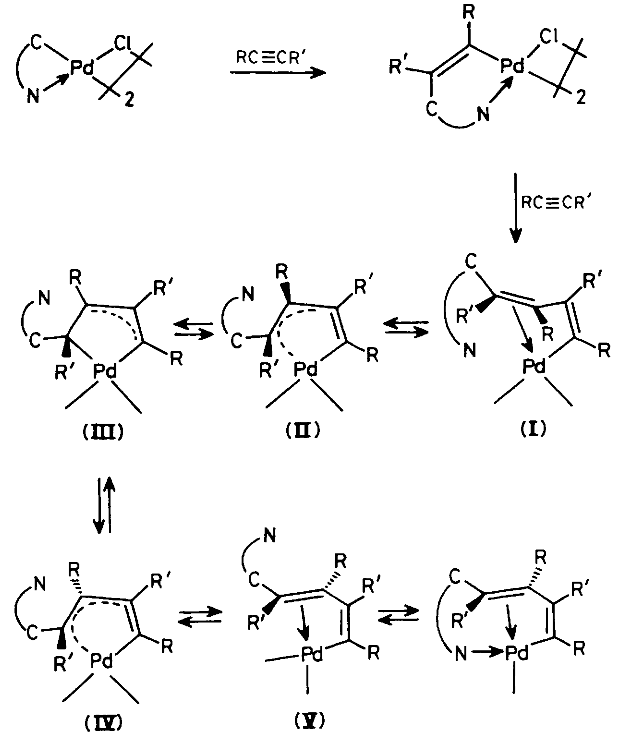
complex (**11**) is stable indefinitely in solution at room temperature. Moreover, its ^1H n.m.r. spectrum is very different from that of (**7**) (no aromatic protons were found at high chemical shifts) and therefore it is likely that the structure of (**11**) must resemble that of previously published[2] expanded (see later) organometallic rings. Complex (**2**) reacted in a similar fashion with two equivalents of ethyl 3-phenylpropionate to afford (**12**) as yellow crystals. An important feature of this latter reaction is that (**12**) is afforded as only one isomer. (The ^1H n.m.r. spectrum of the crude reaction product shows only two signals for the two ethyl groups and two sharp singlets for the C–Me and the N–H units respectively.) We therefore concluded that the insertion of alkynes is regiospecific, a result that is in agreement with most of our previous observations in this field.[2d,3b,4]

It must also be noted that with these alkynes only the bis-insertion products were isolated even when the reaction was performed with different stoicheiometries (*i.e.* with Pd:alkyne ratios different from 1:2). It was thus impossible to obtain a compound in which only one alkyne was inserted into the Pd–C bond of (**2**). In order to unambigously determine the geometry of these molecules a single crystal *X*-ray diffraction study was undertaken on (**12**). An ORTEP diagram, together with the numbering system of the atoms, is shown in Figure 2. Selected interatomic distances and angles are given in Table 2.

Table 2. Selected interatomic distances (Å) and bond angles (°) for compound (**12**)

Pd–Cl	2.3281(6)	N(1)–C(21)	1.304(3)
Pd–C(7)	2.140(2)	N(2)–C(21)	1.341(3)
Pd–C(8)	2.164(2)	C(10)–C(17)	1.340(3)
Pd–C(10)	1.989(2)	C(7)–C(8)	1.415(3)
Pd–N(1)	2.182(2)	C(8)–C(17)	1.504(3)
N(1)–Pd–Cl	100.82(5)	C(10)–Pd–Cl	96.78(7)
C(8)–Pd–N(1)	92.11(7)	C(10)–Pd–C(8)	67.38(8)
C(10)–Pd–C(7)	85.54(8)	C(71)–C(7)–C(6)	112.5(2)
C(8)–C(7)–C(6)	125.2(2)	N(2)–C(21)–N(1)	116.5(2)
C(7)–Pd–N(1)	81.22(7)		

The insertion of two ethyl 3-phenylpropionate molecules into the Pd–C bond of (**2**) gives rise to a new five-electron donor ligand, which is linked to the palladium centre *via* one nitrogen atom [N(1)], one carbon atom [C(10)], and an η^2-bonded carbon–carbon double bond [C(7)=C(8)]. Including the chlorine atom, this results in a distorted square-planar co-ordination environment around the metal. The metallocyclic unit consists of an eight-membered ring in which the nitrogen atom is located *trans* to the σ-bonded carbon. As in compound (**9**) we observed a tautomerism as the hydrogen atom has migrated from N(1) to N(2) and forms an hydrogen bond with the chlorine atom [N(2)–H(1) 1.02(4) Å, Cl ··· H(1) 2.23(4) Å, N(2)–H(1) ··· 172(3)°]. This study confirms the regiospecificity of the insertion reaction detected by ^1H n.m.r., the two alkynes having coupled to each other in a head-to-tail manner to form the tetrasubstituted butadienediyl chain. Interestingly, the arrangement of the phenyl and the CO_2Et groups on each alkenyl unit is in accordance with those found previously.[2d] Since the palladium–carbon bond is polarized, the metal



Scheme.

obviously bearing a positive charge, this behaviour defines a 'reactivity umpolung'[13] of the alkyne during the insertion.

The stereochemistry around each alkenyl fragment is also noteworthy. The phenyl and CO_2Et substituents of the unit σ-bonded to the palladium are in *cis* position, whereas in the unit η^2-bonded to the metal these groups are *trans* to each other with respect to the C–C double bond. A similar geometry has been previously observed for nine-membered palladocyclic rings obtained *via* a related route,[2d] and for the compound which resulted from the insertion of two diphenylacetylene molecules into the Rh–C bond of orthometallated triphenylphosphine, thus forming another eight-membered metallocyclic ring.[2e] Given the hypothesis that the insertion of two alkyne moieties into the Pd–C bond of (2) occurs in a stepwise fashion, we would expect that the geometry around the butadienyl chain should be *cis* for both C=C bonds. A likely pathway for the isomerisation observed is given in the Scheme. The key intermediate (**III**) in this process contains a palladacyclopentenyl unit,[14] which can evolve either to intermediate (**I**) or (**V**). The driving force for the quantitative formation of (**V**) in our cases is probably due to the better co-ordination ability of the heteroatom in (**V**) than in (**I**) as shown by molecular models.

The reaction between (**2**) and dmad in CH_2Cl_2 was identical to that observed between (**1**) and this alkyne except that the reaction was complete only after 48 h. It afforded almost quantitatively compound (**13**) which was formed by the insertion of three alkynes into the Pd–C bond of (**2**). All the spectroscopic data of (**13**) compare well with those of (**9**) so that it is very likely that these compounds have a similar structure. It is also noteworthy that, once again the formation of (**13**) was independent of the stoicheiometry used.

This study is another example of the great variety of reactions that the Pd–C bonds of cyclopalladated compounds can display towards alkynes. The reactions observed here deviate from those we have previously observed for related complexes in several respects. Thus, the number of alkynes inserted in the Pd–C bonds depends uniquely upon the type of alkyne that was treated with (**1**) or (**2**). Contrary to our previous studies, *stepwise* mono-, di-, or tri-insertion could not be achieved even when various stoicheiometries were used. This, and the rather mild conditions under which the reactions occurred, allowed us to conclude that the Pd–C bonds of the compounds studied in this paper have a higher degree of reactivity than those of the other metallocyclic compounds studied to date in our laboratory and elsewhere. Moreover complex (**1**), which contains the palladated acetanilide ligand, is also significantly more reactive than complex (**2**), containing the palladated amidine unit, since the insertion reactions occurred much faster and under milder conditions for the former than for the latter. This result parallels what we have recently found for a related compound in which the palladocyclic unit contained an oxygen–palladium donor bond of an 8-methoxynaphth-1-yl chelate,[15] and which was shown to have a much higher reactivity compared with all other compounds containing a nitrogen donor atom.

Another interesting feature is the role that the second heteroatom in the metallocyclic unit of the starting materials (**1**) and (**2**) can play. Indeed, after reactions with alkynes this nitrogen atom is now bound to the palladium centre in several instances, as in compounds (**6**), (**9**), (**11**), (**12**), and (**13**). This latter feature might easily be explained by considering that the deco-ordination of the heteroatom in the starting material is likely to take place during insertion of the alkyne into the palladium–carbon bond.[2b] Thus after insertion, the reco-ordination to the palladium centre of the modified ligand will obviously take place at the donative atom that leads to the more thermodynamically stable isomer thus leading to five- or six- rather than seven- or eight-membered organometallic rings.

Experimental

General.—All manipulations were performed under dry, oxygen-free nitrogen using standard techniques. All solvents were dried and distilled under nitrogen prior to use. Infrared (KBr pellets) spectra were recorded in the region 4 000—400 cm^{-1} using a Perkin-Elmer 398 spectrophotometer. The ^1H and ^{13}C-$\{^1H\}$ n.m.r. spectra were recorded at 200.13 and 50.32 MHz, respectively, using a Bruker SY 200 instrument. Proton and carbon chemical shifts (δ/p.p.m., J/Hz), are positive downfield relative to external $SiMe_4$. Elemental analyses were carried out by the Service Central de Microanalyses du C.N.R.S. (Strasbourg, France). Mass spectra were obtained with a Thomson THN 208 instrument.

Syntheses.—Compounds (**1**)[6a] and (**2**)[5] were prepared by published methods. All other reagents were obtained from commercial sources and used as received.

Reaction between (**2**) *and pyridine.* An excess of pyridine (0.79 g, 10 mmol) was added to a suspension of (**2**) (2.8 g, 4 mmol) in dichloromethane (50 cm^3) and stirred for 15 min. The colourless solution thus obtained was filtered on a Celite column (4 cm long) to remove traces of metallic palladium. Compound (**3**) precipitated slowly from this solution as white microcrystals. It was also formed when concentrating the solution under vacuum. It was washed with pentane (3 × 25 cm^3) and dried *in vacuo* (3.1 g, 90%) (Found: C, 53.05; H, 4.35; N, 10.1. $C_{19}H_{18}ClN_3Pd$ requires C, 53.0; H, 4.2; N, 9.8%); ν(NH) 3 000 cm^{-1}. Treating compound (**3**) with aqueous HCl afforded quantitatively compound (**2**).

$[\overline{\text{Pd}(o\text{-C}_6\text{H}_4\text{NHCMe=N}}\text{Ph})(\text{Bu}^t\text{NC})\text{Cl}]$ (**4**). To a yellow-green suspension of (**2**) (1.4 g, 2 mmol) in dichloromethane (40 cm^3) was added t-butyl isocyanide (0.33 g, 4 mmol) to afford after 0.5 h a colourless solution. Traces of palladium metal were

Table 3. Crystal data and intensity data collection of (**9**) and (**12**)

Compound	(**9**)	(**12**)
Empirical formula	$C_{26}H_{26}ClNO_{13}Pd$	$C_{36}H_{33}ClN_2O_4Pd$
M	702.3	699.5
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	8.811(1)	10.647(5)
b/Å	17.105(3)	13.859(3)
c/Å	19.799(4)	14.530(4)
α/°		57.49(2)
β/°	91.45(1)	66.00 (4)
γ/°		71.98(3)
U/Å^3	2 983	1 640
Z	4	2
Crystal size/mm	0.52 × 0.34 × 0.28	0.40 × 0.26 × 0.12
μ(Mo-K_α)/cm^{-1}	7.70	6.82
D_c/g cm^{-3}	1.56	1.42
Reflections collected	5 913 (hkl, $\bar{h}kl$)	6 234 (hkl, $\bar{h}kl$, $hk\bar{l}$, $\bar{h}\bar{k}l$)
Reflections merged	5 240	5 765
Merging factor	1.92	1.41
Reflections used	4 186 [$F > 2\sigma(F)$]	4 908 [$F > 3\sigma(F)$]
F(000)	1 424	716
Average shift/e.s.d. (last cycle)	0.31	0.21
Goodness of fit	1.08	0.86
N_r/V_v	9.1	9.8
Scale factor	1.226	2.045
$R = \Sigma\|\|F_o\| - \|F_c\|/\Sigma/F_o\|$	0.0324	0.0242
$R' = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma wF_o]^{\frac{1}{2}}$	0.0342	0.0277

* Details applicable to both compounds: temperature, 21 ± 1 °C; radiation, Mo-K_α (λ = 0.710 73 Å) (graphite monochromator); scan type, θ—2θ; scan range, 1.5 + 345 tan θ/°; 2θ range, 3—50°; scan speed, depending upon reflection; background, half of scan time, in fixed position, before and after every scan; secondary extinction, non-observed; weighting scheme, $w = w'\{1 - [\Delta F/6\sigma(F)]^2\}^2$; $w' = 1/\sum_{r=1}^{n} AT(X)$ with three coefficients A [5.160, −2.206, 4.077 for compound (**9**), and 3.851, −0.716, 2.637 for compound (**12**)] for the Chebyshev series $T(X)$, where $X = F_c/F_c$ (max.) (E. Prince, 'Mathematical Techniques in Crystallography,' Springer Verlag, Berlin, 1982); N_r = number of reflections used, N_v = number of variable parameters.

Table 4. Fractional atomic co-ordinates for the heavy atoms of compound (**9**)*

Atom	X/a	Y/b	Z/c
Pd	0.263 46(2)	0.073 67(1)	0.139 47(1)
Cl	0.155 0(1)	0.084 22(5)	0.028 04(4)
N(1)	0.482 0(3)	0.049 1(1)	0.117 1(1)
C(1)	0.558 2(4)	0.082 8(2)	0.070 7(2)
C(11)	0.725 8(4)	0.093 9(2)	0.068 8(2)
O(11)	0.486 7(3)	0.115 5(2)	0.018 8(1)
C(2)	0.554 6(3)	0.009 3(2)	0.172 9(2)
C(3)	0.676 5(4)	−0.041 2(2)	0.167 2(2)
C(4)	0.737 4(4)	−0.076 6(2)	0.224 6(2)
C(5)	0.679 0(3)	−0.061 5(2)	0.286 7(2)
C(6)	0.553 6(3)	−0.013 3(2)	0.292 5(2)
C(7)	0.488 0(3)	0.021 7(1)	0.235 4(1)
C(21)	0.349 4(3)	0.071 9(2)	0.235 3(1)
C(211)	0.370 2(3)	0.158 3(2)	0.240 7(1)
O(211)	0.271 0(2)	0.202 7(1)	0.257 3(1)
O(212)	0.508 0(2)	0.181 7(1)	0.222 9(1)
C(212)	0.526 6(5)	0.265 6(2)	0.217 8(3)
C(22)	0.215 7(3)	0.046 7(1)	0.280 9(1)
C(221)	0.074 9(3)	0.086 8(1)	0.250 0(1)
O(221)	0.060 6(2)	0.096 8(1)	0.188 80(9)
O(222)	−0.028 3(2)	0.104 8(1)	0.292 82(9)
C(222)	−0.164 4(4)	0.143 8(2)	0.266 2(2)
C(31)	0.238 7(3)	0.066 9(2)	0.355 8(1)
C(311)	0.283 9(6)	0.144 4(2)	0.383 8(2)
O(311)	0.185 9(5)	0.188 9(2)	0.406 0(1)
O(312)	0.426 9(4)	0.157 1(2)	0.384 6(2)
C(312)	0.451(1)	0.238 0(5)	0.421 4(6)
C(313)	0.289(2)	0.256 3(6)	0.431 5(6)
C(32)	0.212 2(3)	0.003 8(2)	0.393 8(1)
C(321)	0.226 6(4)	0.002 6(2)	0.468 9(1)
O(321)	0.291 3(5)	0.051 0(2)	0.501 6(1)
O(322)	0.159 0(3)	−0.058 5(2)	0.493 9(1)
C(322)	0.171 1(6)	−0.069 4(3)	0.566 1(2)
C(41)	0.170 2(3)	−0.062 0(2)	0.350 2(1)
C(411)	0.128 3(3)	−0.141 4(2)	0.376 8(1)
O(411)	0.219 5(3)	−0.189 2(1)	0.394 3(1)
O(412)	−0.019 3(2)	−0.147 7(1)	0.380 0(1)
C(412)	−0.076 7(5)	−0.220 8(2)	0.406 3(3)
C(42)	0.178 2(3)	−0.040 9(1)	0.285 3(1)
C(421)	0.145 8(3)	−0.098 0(2)	0.230 6(1)
O(421)	0.122 6(4)	−0.164 9(1)	0.241 5(1)
O(422)	0.135 9(4)	−0.067 6(1)	0.170 7(1)
C(422)	0.104 4(7)	−0.121 5(3)	0.114 8(2)

* The CO_2Me group attached to C(31) is disordered; the O(312), C(312), O(311), and C(313) atoms are in statistical distribution on two sites related to each other by a pseudo-two-fold axis through the C(31)–C(311) bond, with assigned occupation factors in the ratio 60:40 for C(312) and C(313) respectively.

removed by filtration on a Celite column (4 cm long). This solution was concentrated to *ca.* 5 cm^3 under reduced pressure and addition of pentane (50 cm^3) led to the quantitative precipitation of (**4**), which was washed with pentane and dried *in vacuo* (1.6 g, 92%) (Found: C, 52.75; H, 5.2; N, 9.9. $C_{19}H_{22}ClN_3Pd$ requires C, 52.55; H, 5.1; N, 9.7%); ν(NH) 3 280, ν(C≡N) 2 190 cm^{-1}; δ_H($CDCl_3$): 8.18 (1 H, s, NH), 7.46—6.82 (9 H, m, aromatic), 2.01 (3 H, s, Me), and 1.41 (9 H, s, Bu^t).

$[\{\overline{Pd[C(CF_3)=C(CF_3)(o\text{-}C_6H_4NHCMe=O})](\mu\text{-}Cl)\}_2]$ (**5**). An excess of hexafluobut-2-yne (0.16 g, 1 mmol) was condensed at liquid nitrogen temperature into a suspension of (**1**) (0.15 g, 0.27 mmol) in dichloromethane (20 cm^3). The reaction mixture was allowed to attain room temperature. After stirring for 17 h the unreacted starting material was filtered off and the yellow solution thus obtained was concentrated under reduced pressure to 4 cm^3. Addition of pentane (30 cm^3) afforded a yellow solid which was collected by filtration, washed with pentane (2 × 10 cm^3), and dried *in vacuo* (0.11 g, 47%) (Found: C, 33.05; H, 1.8; N, 2.85. $C_{12}H_8ClF_6NOPd$ requires C, 32.9; H, 1.85, N, 3.2%); ν(NH) 3 212, ν(C=O) 1 608 and 1 590 cm^{-1}; δ_H($CDCl_3$): 9.27 and 9.11 (2 H, 2 × s, NH); 7.45—6.88 (8 H, m, aromatic); 1.87 and 1.82 (6 H, 2 × s, Me).

$[\overline{Pd[C(CF_3)=C(CF_3)(o\text{-}C_6H_4NHCMe=O})](py)Cl]$ (**6**). To a yellow solution of (**5**) (0.1 g, 0.23 mmol), an excess of pyridine (0.04 g, 0.5 mmol) was added to afford immediately a colourless solution which was concentrated to *ca.* 5 cm^3 under reduced pressure. Addition of pentane (30 cm^3) caused the quantitative precipitation of (**6**). This compound could be obtained as light yellow crystals from a CH_2Cl_2–hexane solution (0.21 g, 90%) (Found: C, 39.75; H, 2.25; N, 5.6. $C_{17}H_{13}ClF_6N_2OPd$ requires C, 39.5; H, 2.55; N, 5.4%); ν(NH) 3 320, ν(CO) 1 698 cm^{-1}; δ_H($CDCl_3$): 9.34 and 8.92 (2 H, 2 × s, NH); 8.83—6.44 (18 H, m, aromatic); 2.35 and 1.28 (6 H, 2 × s, Me).

Reaction between (**1**) *and diphenylacetylene.* A suspension of (**1**) (0.28 g, 0.5 mmol) and diphenylacetylene (0.8 g, 4.5 mmol) in dichloromethane was stirred for 2 h after which time (**1**) had dissolved. The yellow-orange solution thus obtained was filtered on a Celite column (4 cm long) and concentrated to *ca.* 3 cm^3 under reduced pressure. Addition of pentane (30 cm^3) led to the precipitation of (**7**) which was washed with pentane (3 × 15 cm^3) and dried *in vacuo* (0.55 g, 87%) (Found: C, 67.95; H, 4.5; N, 1.95. $C_{36}H_{28}ClNOPd$ requires C, 68.35; H, 4.45; N,

Table 5. Fractional atomic co-ordinates for the heavy atoms of compound (**12**)*

Atom	*X/a*	*Y/b*	*Z/c*
Pd	0.362 13(2)	0.169 48(1)	0.157 33(1)
Cl	0.561 08(6)	0.049 55(6)	0.200 23(6)
N(1)	0.328 2(2)	0.109 0(2)	0.059 1(2)
C(1)	0.273 3(2)	0.203 3(2)	−0.029 0(2)
C(2)	0.281 5(3)	0.201 2(2)	−0.126 3(2)
C(3)	0.244 0(3)	0.299 9(3)	−0.215 7(2)
C(4)	0.196 0(3)	0.401 2(3)	−0.210 3(2)
C(5)	0.184 8(3)	0.404 5(2)	−0.113 7(2)
C(6)	0.224 2(2)	0.305 6(2)	−0.022 7(2)
C(7)	0.224 3(2)	0.313 4(2)	0.076 6(2)
C(71)	0.286 3(2)	0.418 2(2)	0.038 9(2)
O(71)	0.399 9(2)	0.438 9(2)	−0.026 5(2)
O(72)	0.198 8(2)	0.486 5(1)	0.080 9(2)
C(72)	0.254 9(3)	0.587 8(2)	0.049 6(3)
C(73)	0.155 7(4)	0.643 5(4)	0.117 5(4)
C(8)	0.149 9(2)	0.247 7(2)	0.192 3(2)
C(81)	0.046 5(2)	0.172 6(2)	0.230 5(2)
C(82)	−0.045 6(2)	0.206 2(2)	0.170 2(2)
C(83)	−0.140 7(3)	0.134 1(3)	0.206 7(3)
C(84)	−0.146 2(3)	0.030 6(3)	0.303 1(3)
C(85)	−0.057 2(4)	−0.002 4(3)	0.364 3(3)
C(86)	0.039 3(3)	0.067 7(2)	0.329 2(2)
N(2)	0.374 2(2)	−0.078 4(2)	0.178 5(2)
C(21)	0.308.1(2)	0.002 8(2)	0.102 1(2)
C(22)	0.371 4(2)	−0.199 9(2)	0.242 3(2)
C(23)	0.355 5(4)	−0.251 6(3)	0.357 2(3)
C(24)	0.364 2(4)	−0.370 6(3)	0.421 4(3)
C(25)	0.388 2(4)	−0.435 5(3)	0.370 7(3)
C(26)	0.405 2(3)	−0.384 9(2)	0.256 0(3)
C(27)	0.396 8(3)	−0.266 3(2)	0.191 0(2)
C(28)	0.209 2(3)	−0.033 5(2)	0.079 7(3)
C(10)	0.317 0(2)	0.231 2(2)	0.264 5(2)
C(11)	0.409 4(2)	0.234 4(2)	0.314 6(2)
C(12)	0.415 7(3)	0.153 1(3)	0.423 8(2)
C(13)	0.507 0(4)	0.159 9(3)	0.466 1(3)
C(14)	0.591 6(4)	0.245 6(3)	0.400 0(3)
C(15)	0.585 4(3)	0.325 1(3)	0.293 0(3)
C(16)	0.495 8(3)	0.319 4(2)	0.250 1(2)
C(17)	0.180 8(2)	0.259 9(2)	0.277 5(2)
C(18)	0.069 3(3)	0.300 7(2)	0.354 4(2)
O(18)	−0.048 7(2)	0.326 3(2)	0.354 7(2)
O(19)	0.144 6(2)	0.303 7(2)	0.425 5(2)
C(19)	0.012 4(5)	0.341 4(4)	0.506 2(4)
C(20)	0.074 2(7)	0.318 5(5)	0.588 6(4)

2.2%); ν(NH) 3 413, ν(C=O) 1 700 cm^{-1}; δ_H(CD$_2$Cl$_2$, −80 °C): 11.10 (1 H, s, NH); 7.56—6.40 (20 H, m, aromatic); 5.27 and 4.76 (4 H, 2 br m); 2.0 (3 H, s, Me); δ_C(CD$_2$Cl$_2$, −40 °C): 168.8 (C=O); 147.8, 142.3, 140.7, 134.0, 128.0, 122.0, 111.8, 94.4, and 69.1; 24.6 (Me).

C$_{10}$H$_3$Ph$_4$(NHCMe=O) (**8**). A suspension of (**1**) (0.28 g, 0.5 mmol) and diphenylacetylene (0.8 g, 4.5 mmol) in chlorobenzene (50 cm^3) was refluxed during 0.5 h. The black solution thus obtained was evaporated under reduced pressure and compound (**8**) was extracted with diethyl ether (75 cm^3). This solution was filtered on an alumina column and concentrated under reduced pressure. Addition of hexane afforded compound (**8**) as yellow crystals (0.72 g, 74%) (Found: C, 88.05; H, 5.45; N, 2.95%; M^+, 489. C$_{36}$H$_{27}$NO requires C, 88.3; H, 5.55; N, 2.85%; *M*, 489); ν(C=O) 1 662, ν(NH) 3 280 cm^{-1}; δ_H(CDCl$_3$); 8.27—6.31 (24 H, m, aromatic + NH) and 1.72 (3 H, s, CH$_3$).

[Pd{C(CO$_2$Me)[C(CO$_2$Me)C(CO$_2$Me)=C(CO$_2$Me)C(CO$_2$-Me)=C(CO$_2$Me)][*o*-C$_6$H$_4$N=CMe(OH)]}Cl] (**9**). To a suspension of (**1**) (0.25 g, 0.45 mmol) in dichloromethane (30 cm^3), dimethyl acetylenedicarboxylate (0.43 g, 3 mmol) was added and the reaction mixture stirred, at room temperature, for 3 h. The volume of the solvent was reduced under vacuum (to *ca.* 5 cm^3) and addition of pentane (40 cm^3) led to formation of a yellow solid which was collected by filtration, washed with pentane (2 × 15 cm^3), and dried *in vacuo* (0.3 g, 95%). Complex (**9**) was obtained as orange-yellow crystals from an acetone–pentane solution (Found: C, 44.35; H, 3.8; N, 1.9. C$_{26}$H$_{26}$Cl-NO$_{13}$Pd requires C, 44.45; H, 3.75; N, 2.0%); ν(OH) 2 960 cm^{-1}; δ_H(CDCl$_3$): 11.7 (1 H, s, OH); 7.08—6.76 (4 H, m, aromatic); 3.97, 3.96, 3.82, 3.78, 3.77, and 3.67 (18 H, 6 × s, CO$_2$Me); 2.23 (3 H, s, CMe).

o-C$_6$H$_4$(NHCMe=O)CH=CH(C$_5$Me$_5$) (**10**). A mixture of (**1**) (0.56 g, 1.0 mmol) and but-2-yne (0.54 g, 10 mmol) in chlorobenzene (25 cm^3) was stirred for 1.5 h after which time compound (**1**) had dissolved. The orange-brown solution thus obtained was refluxed for 0.4 h. The solvent was evaporated and the orange-brown residue redissolved in diethyl ether (75 cm^3) and filtered on an alumina column (4 cm long) to afford a light-yellow solution which was evaporated to dryness to give (**10**) as a white powder (0.54 g, 91%); this compound was crystallized as white crystals by slow evaporation of a diethyl ether–pentane (1:2) solution (Found: C, 81.15; H, 8.65; N, 4.7%; M^+, 295. C$_{20}$H$_{25}$NO requires C, 81.3; H, 8.5; N, 4.7%; *M*, 295); ν(NH) 3 220, ν(C=O) 1 645 cm^{-1}; δ_H(CD$_2$Cl$_2$): 7.72—7.00 (5 H, m, aromatic + NH); 6.39 and 5.39 (2 H, 2 × d, 2 CH, $^2J_{HH}$ 16.0); 2.11 and 1.09 (6 H, 2 × s, Me), 1.76 and 1.68 (12 H, 2 × s, Me).

[Pd{C(Ph)=C(Ph)C(Ph)=C(Ph)(*o*-C$_6$H$_4$N=CMeNHPh)}Cl] (**11**). A mixture of (**2**) (0.7 g, 1 mmol) and diphenylacetylene (0.8 g, 4.5 mmol) in chlorobenzene (60 cm^3) was heated at reflux for 3 h. The orange-brown solution was evaporated to dryness and washed with pentane (4 × 20 cm^3) to remove the excess of diphenylacetylene. The yellow-orange solid was dissolved in dichloromethane (50 cm^3) and filtered on a Celite column (4 cm long) to remove traces of palladium metal and concentrated to *ca.* 5 cm^3 under reduced pressure. Addition of pentane (50 cm^3) gave a yellow solid which was collected by filtration, washed with pentane (3 × 15 cm^3) and dried *in vacuo* (1.2 g, 85%). The yellow crystalline product was obtained from a CH$_2$Cl$_2$–hexane solution [Found: C, 69.85; H, 4.7; N, 3.55. C$_{42}$H$_{33}$ClN$_2$Pd·0.25CH$_2$Cl$_2$ (detected by ^{1}H n.m.r.) requires C, 69.6; H, 4.65; N, 3.85%); ν(NH) 3 020 cm^{-1}; δ_H(CDCl$_3$): 10.50 (1 H, s, NH); 7.92—6.47 (29 H, m, aromatic); 1.23 (3 H, s, Me).

[Pd{C(Ph)=C(CO$_2$Et)C(Ph)=C(CO$_2$Et)(*o*-C$_6$H$_4$N=CMe-NHPh)}Cl] (**12**). To a suspension of (**1**) (0.37 g, 0.53 mmol) in chlorobenzene (40 cm^3), ethyl 3-phenylpropionate (0.44 g, 2.5 mmol) was added and the reaction mixture refluxed for 4 h. The yellow-brown suspension was filtered on a Celite column (3 cm long) to remove traces of palladium metal. The orange solution thus obtained was concentrated under reduced pressure to *ca.* 4 cm^3; pentane (30 cm^3) was added to give a yellow solid which was removed by filtration, washed with pentane (3 × 15 cm^3), and dried *in vacuo* (0.57 g, 77%). The yellow crystalline product was obtained from a CH$_2$Cl$_2$–pentane solution at room temperature (Found: C, 62.4; H, 4.7; N, 3.45. C$_{36}$H$_{33}$ClN$_2$O$_4$Pd requires C, 61.8; H, 4.75; N, 4.0%); ν(NH) 2 980 cm^{-1}; δ_H(CDCl$_3$): 10.47 (1 H, s, NH); 7.80—6.49 (19 H, m, aromatic); 4.28 and 3.91 (4 H, 2 × m, CO$_2$CH_2CH$_3$); 1.21 and 0.87 (6 H, 2 × t, CO$_2$CH$_2$CH_3, $^3J_{HH}$ 8.3); 1.23 (3 H, s, Me).

[Pd{C(CO$_2$Me)[C(CO$_2$Me)C(CO$_2$Me)=C(CO$_2$Me)C(CO$_2$-Me)=C(CO$_2$Me)](*o*-C$_6$H$_4$N=CMeNHPh)}Cl] (**13**). A mixture of (**2**) (0.37 g, 0.53 mmol) and dimethyl acetylenedicarboxylate (0.57 g, 4 mmol) in CH$_2$Cl$_2$ (50 cm^3) was stirred for 48 h at room temperature. The yellow suspension was filtered and the resulting solution concentrated to *ca.* 4 cm^3 under reduced pressure. Addition of hexane gave a yellow-orange solid which was recovered by filtration, washed with hexane, and dried *in vacuo* (0.63 g, 77%) (Found: C, 49.0; H, 4.0; N, 3.65. $C_{32}H_{31}ClN_2O_{12}Pd$ requires C, 49.45; H, 4.0; N, 3.6%); ν(NH) 3 042 cm^{-1}; δ_H($CDCl_3$): 10.87 (1 H, s, NH); 7.40—6.67 (9 H, m, aromatic); 3.96, 3.83, 3.82, 3.79, 3.77, and 3.71 (18 H, 6 × s, CO_2Me); 2.10 (3 H, s, Me).

X-*Ray Study*.—For compounds (**9**) and (**12**), preliminary unit-cell dimensions and symmetry information were derived from precession photographs; each crystal was then set up on a Nonius CAD4 diffractometer. Accurate cell dimensions and orientation matrices were obtained from least-squares refinements of the setting angles of 25 well centred reflections ($30 < 2\theta < 32°$).

Crystal data and data collection parameters are listed in Table 3. Intensities of two standard reflections were monitored every hour and showed no appreciable change during data collections; ψ-scan curves showed no significant intensity variations, and absorption corrections were not applied.

Computations were performed using the CRYSTALS system[16] adapted on a Vax 11/725 computer. Atomic scattering factors for neutral Pd, Cl, N, O, C, and H were taken from International Tables;[17] anomalous dispersion was taken into account.

In both compounds the position of the Pd atom was determined by Harker vector analysis of three-dimensional Patterson maps. All remaining non-hydrogen atoms were found by successive electron-density map calculations. Final refinement was by least squares with a large block approximation to the normal matrix (with all non-hydrogen atoms anisotropic). Hydrogen atoms were located on a difference electron-density map; their atomic co-ordinates were refined with isotropic thermal parameters. The criteria for a satisfactory completed analysis were the average shift to standard deviations (Table 3) and no significant features in the final difference maps. Main features of the refinement appear in Table 3.

Atomic co-ordinates are given in Tables 4 and 5. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank Dr. M. Luke for his comments on the manuscript, Professor Y. Jeannin for providing facilities for determining the *X*-ray structures, the CNPq (Brazil) for a fellowship (to J. D.), the Comptoir Lyon Alemand Louyot for a generous loan of palladium, and the Commission of European Communities for financial support [contract no. ST 2J-0090-1-F(CD)].

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Received 5th October 1987; *Paper* 7/1775