Reactivity of Cyclopalladated Compounds. Part 7.[1] Syntheses of Metallobicyclic Compounds and their Reactions with Acetylenes. *X*-Ray Crystal and Molecular Structures of the Compounds $[(NMe_2CH_2C_6H_4)Pd\{C(CF_3)=C(CF_3)(C_6H_4CH_2NMe_2)\}]$ and $[\{(NMe_2CH_2C_6H_4)C(CF_3)=C(CF_3)\}Pd\{C(CF_3)=C(CF_3)(CH_2C_9H_6N)\}]$ †

Christian Arlen and Michel Pfeffer *
Laboratoire de Chimie de Coordination, Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cédex, France
Odile Bars and Daniel Grandjean
Laboratoire de Cristallochimie, Avenue du Général Leclerc, F-35042 Rennes Cédex, France

Hexafluorobut-2-yne (hfb) reacted with $[M(dmba - H)_2]$ (dmba = *NN*-dimethylbenzylamine, M = Ni or Pd) to give $[(NMe_2CH_2C_6H_4)M\{C(CF_3)=C(CF_3)(C_6H_4CH_2NMe_2)\}]$ compounds in which one acetylene was formally inserted into one of the M–C bonds, the second metallocycle being unmodified. A *cis* geometry has been tentatively assigned to the compound where M = Ni, whereas a *trans* configuration is found for M = Pd. This latter complex isomerizes slowly in solution to give the *cis* isomeric form which has been studied by single-crystal *X*-ray diffraction measurements; the complex crystallizes in the monoclinic space group $P2_{1/n}$ with $a = 11.705(2)$, $b = 11.146(2)$, $c = 16.317(5)$ Å, $\beta = 93.16(2)°$, and $Z = 4$. The two nitrogen atoms are indeed mutually *cis* to each other, the Pd–N distances being rather long [2.231(3) and 2.223(3) Å]; the phenyl ring which is a part of the seven-membered palladated ring is now perpendicular to the co-ordination plane of the Pd atom. Reaction of lithiated *NN*-dimethylnaphthylamine (dmna) or *NN*-dimethylaminotoluene (dmat) with $[PdCl_2(SEt_2)_2]$ gave the bicyclic compounds $[Pd(dmna - H)_2]$ and $[Pd(dmat - H)_2]$, the latter in very low yield however. The former compound gave metallic Pd and an organic product by reaction with hfb. Asymmetric bicyclic compounds have been synthesized by reaction of lithiated dmna, dmat, or dmba with the chlorine-bridged dimers $[\{Pd(dmba - H)Cl\}_2]$ or $[\{Pd(8Me\text{-}quin - H)Cl\}_2]$ (8Me-quin = 8-methylquinoline). Reaction between hfb and the bicyclic compound [Pd(dmba − H)(dmna − H)] afforded a compound in which again only one acetylene has reacted with the Pd–C bond of the palladated dmba moiety; the two Pd–C bonds are *trans* to each other and it also isomerizes into the corresponding *cis* species in solution. [Pd(dmba − H)(8Me-quin − H] with hfb gave a product in which the acetylene reacted with both Pd–C bonds affording a bicyclic compound with two seven-membered rings attached to the same palladium. This product exists as a mixture of *cis* and *trans* isomers but only the *cis* species has been isolated in a pure crystalline form. Its stereochemistry has been confirmed by an *X*-ray diffraction study; the complex crystallizes in the monoclinic space group $P2_{1/n}$ with $a = 13.948(8)$, $b = 12.338(7)$, $c = 16.868(6)$ Å, $\beta = 107.89(4)°$, and $Z = 4$. The seven-membered ring containing the dmba ligand resembles that described above whereas the new ring containing 8Me-quin − H is mainly described by two planes whose dihedral angle is 112.3°. [Pd(dmba − H)(8Me-quin − H)] also reacts under smooth conditions with $MeO_2CC{\equiv}CCO_2Me$ to give a mixture of products from which one compound has been isolated in a pure form: it has fixed one acetylene per palladium atom and we suggest on the basis of n.m.r. data that it has reacted with the C–Pd bond of the palladated 8Me-quin moiety.

We have already shown that the Pd–C σ bonds of dimeric halogen-bridged cyclopalladated compounds containing a nitrogen as the donor atom react readily with substituted acetylenes. Thus one or two acetylenes are formally inserted into these bonds giving rise to seven- or nine-membered rings respectively.[2] We have now studied the reactivity of related monomeric molecules in which two nitrogen-containing cyclometallated ligands are bound to the same metal, towards the insertion reaction of acetylenes into the M–C bonds in order hopefully to obtain information regarding the detailed mechanism of the reaction.

Such metallobicyclic compounds (1) have been known since 1972 and were first synthesized by Chini and co-workers [3] with metals of the nickel triad. On the other hand, asymmetric metallobicyclic compounds have been prepared by reacting lithiated ligands with chlorine-bridged cyclopalladated dimers.[4] To our knowledge, the chemistry of these compounds is scarce and very little is known about the reactivity of their metal–carbon σ bonds. In this paper we report the synthesis of symmetrical and asymmetrical metallobicyclic compounds and describe their reactivity with acetylenes.

Results and Discussion

Synthesis of the Bicyclic Compounds.—The new symmetrical bicyclic compounds (2a) and (2b) have been pre-

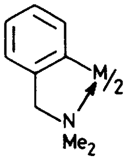
---

† [(*o*-Dimethylaminomethyl)phenyl-*C*,*N*]{3-[(*o*-dimethylaminomethyl)phenyl]hexafluorobut-2-en-2-yl-*C*²,*N*}palladium and {3-[(*o*-Dimethylaminomethyl)phenyl]hexafluorobut-2-en-2-yl-*C*²,*N*}[3-(8′-quinolylmethyl)hexafluorobut-2-en-2-yl-*C*²,*N*)]palladium respectively.

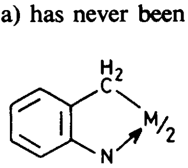
Supplementary data available (No. SUP 23587, 40 pp.): structure factors, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

pared by the reaction of two equivalents of lithiated *o-NN*-dimethylaminotoluene (dmat) with $[MCl_2(SEt_2)_2]$. The synthesis of compound (2b) has been independently reported very recently.[5] Surprisingly we could only obtain very low yields of the palladium analogue (2a).

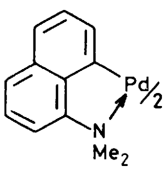
To our knowledge the lithiation reaction of *NN*-dimethyl-1-naphthylamine (dmna) has never been reported in the literature. However the reaction of n-butyl-lithium with dmna in a diethyl ether–hexane solution affords a high yield of a white solid. Its ^{13}C and ^{1}H n.m.r. spectra reveal that this compound is a 1 : 1 solvate of diethyl ether and that the two methyl groups are diastereotopic. This species is thus probably a polynuclear species similar to that found recently for lithiated *NN*-dimethylbenzylamine (dmba) which is a tetranuclear compound in weakly co-ordinating solvent and a binuclear species in tetrahydrofuran (thf).[6] The reaction of $[\{Li(dmna\text{-}H)\}_n \cdot nEt_2O]$ * with $[PdCl_2(SEt_2)_2]$ affords a good yield of compound (3).



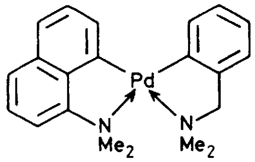
(1a) M = Ni
(1b) M = Pd
(1c) M = Pt



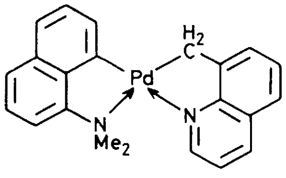
(2a) M = Pd
(2b) M = Pt



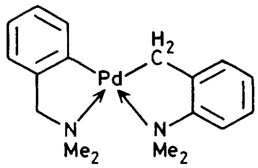
(3)



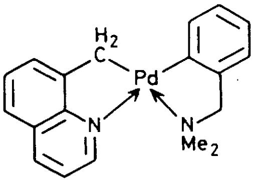
(4)



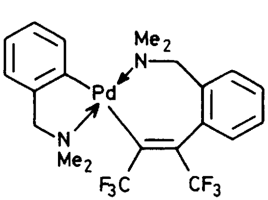
(5)



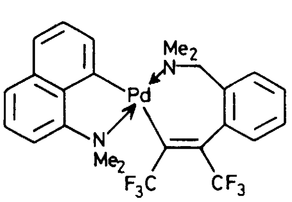
(6)



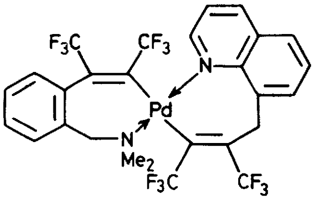
(7)



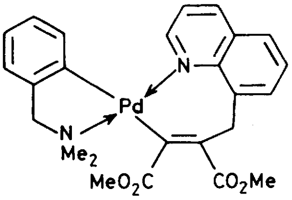
(8)



(10)



(13)



(14)

The n.m.r. data for compounds (2a) and (3) indicate a planar co-ordination around palladium for both and suggest that these species exist as only one isomeric form in solution. By analogy to compound (1b) whose stereochemistry has been well established we propose a *cis* configuration for (2a) and (3).

The new asymmetric bicyclic compounds (4)—(7) have been synthesized by reacting lithiated ligands with chlorine-bridged cyclopalladated compounds. Thus compounds (4) and (6) were obtained by the reaction of lithiated dmna and dmat respectively with $[\{Pd(dmba - H)Cl\}_2]$[7] whereas (5) and (7) were prepared by the reaction of lithiated dmna and dmba with $[\{Pd(8Me\text{-}quin - H)Cl\}_2]$ (8Me-quin = 8-methylquinoline).[8] Compound (6) however, has not been obtained in a pure form because the reaction of lithiated dmat with $[\{Pd(dmba - H)Cl\}_2]$ occurs with some decomposition and therefore (6) was always obtained together with some amounts of (1b). We could not separate these two compounds due to their similar solubilities in the common organic solvents. Reaction of lithiated dmat with $[\{Pd(8Me\text{-}quin - H)Cl\}_2]$ gave only decomposition products and a bicyclic compound for example, [Pd(8Me-quin — H)(dmat — H)] could not be synthesized. This result parallels the difficult synthesis of $[Pd(dmat - H)_2]$ (see above); we therefore believe that in this type of bicyclic compound two benzylic carbons are too ' soft ' for the palladium atom and that the stabilization of the molecule by the formation of metallocycles with Pd–N bonds is probably too small. These results are to be compared with phosphorus-containing ligands for which it is indeed possible to synthesize metallobicyclic compounds with two benzylic carbons with metals of the nickel triad.[9]

Again the n.m.r. for compounds (4)—(7) suggest planar co-ordination around palladium and the presence of only one type of isomer. We propose that the *cis* configuration is the most likely for the following reasons: an *X*-ray diffraction study of a related bicyclic compound [Pd(8Me-quin — H)-(1MeO-np — H)] (1MeO-np = 1-methoxynaphthalene) revealed that the C–Pd bonds are indeed *cis* to each other.[10] Compounds (5) and (7) have a similar geometry since the ^{1}H and ^{13}C n.m.r. chemical shifts for the CH_2 groups are close to those found for the previous compound. We also show later that for these bicyclic compounds the *cis* geometry is the most stable configuration (see below) and therefore it is unlikely that these stable compounds are *trans* isomers.

Reactions with Acetylenes.—Symmetrical bicyclic compounds (1)—(3). Neither the *cis* nor the *trans* platinum compound (1c)[3] reacts with hexafluorobut-2-yne (hfb) even after one week at 70 °C. However treatment of compound (2b) with hfb in a thf solution gives a yellow solution. Removal of the solvent gave a compound which we were unable to purify. In the i.r. spectrum of the product, however, an absorption was observed at *ca.* 1 980 cm^{-1} which can be assigned to the stretching frequency of a C≡C bond weakly co-ordinated to platinum.[11] This compound was unstable and lost its acetylene rather quickly leading to some decomposition products which we could not fully characterize.

The palladium analogue of (1c), complex (1b) reacts smoothly with an excess of hfb to give the yellow crystalline compound (8). The i.r. spectrum shows typical absorptions for the dmba ligand together with new ones typical of hfb inserted into a Pd–C bond.[2] The ^{1}H n.m.r. spectrum indicates that the total symmetry of the molecule is now lower than in

---

* *Note added in proof:* the *X*-ray structure of this compound has been obtained after submission of this paper. It shows it to be dimeric ($n = 2$), with the Et_2O molecules bound to the Li atoms (J. T. B. H. Jastrzebski, G. Van Koten, K. Goubitz, C. Arlen, and M. Pfeffer, *J. Organomet. Chem.*, 1983, **246**, C75).

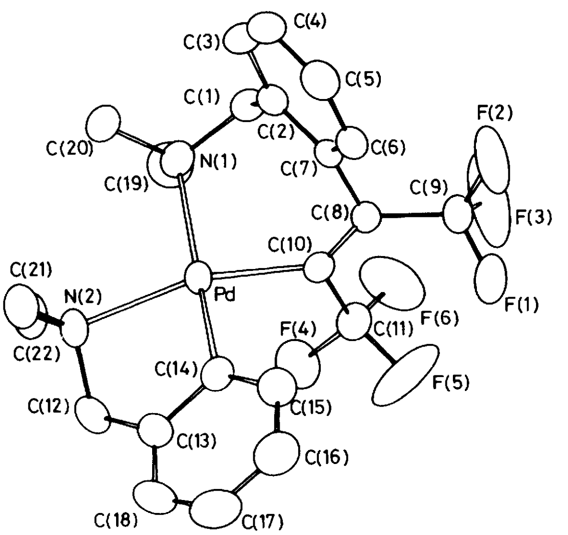


Figure 1. ORTEP drawing of compound (9a). All hydrogen atoms have been omitted for clarity

(1b) since four signals are observed for the methyl protons together with two four-line AB patterns for the CH_2 protons. The ^{19}F n.m.r. spectrum reveals the presence of two different CF_3 groups.[2]

These results together with the analytical data suggest that despite the presence of an excess of hfb one acetylene only has reacted with one C–Pd of (1b) and that a new bicyclic molecule with a seven-membered ring has been formed. Compound (8) isomerizes slowly in a CH_2Cl_2 solution to give white crystals of (9a) with spectroscopic data slightly different from those of (8). This isomerization process is accelerated in the presence of CO (see Experimental section). Compounds (8) and (9a) are thus *trans* and *cis* isomers. An *X*-ray diffraction study has been carried out on (9a) in order to establish its stereochemistry and to determine the geometry of the seven-membered ring.

The molecular structure of (9a) is shown in Figure 1 which also shows the crystallographic numbering system. The molecular packing in the unit cell is given in Figure 2. Interatomic distances and angles are given in Table 1, fractional atomic co-ordinates in Table 3, least-squares planes in Table 4, and crystal data in Table 7.

It is at once apparent that one acetylene has indeed been inserted into one Pd–C bond, giving rise to a seven-membered ring including Pd. The Pd–C bonds are *cis* to each other, and therefore compound (8) must be the *trans* isomer. The geometry around the palladium atom can be described as distorted square planar (see plane 1, Table 4). The two N–Pd bonds are rather long ($\gtrsim$2.22 Å) because of the large *trans* influence of the two C–Pd bonds. The puckering of the ring of the non-reacted dmba (see plane 6, Table 4) is a normal feature for cyclometallated benzylamines.[12] The seven-membered ring on the other hand has adopted a boat conformation; the dihedral angle between the planes defined by Pd, N(1), and C(10) and the four remaining atoms, *i.e.* C(1), C(2), C(7), C(8), is 86.3° (Table 4). The distance of the carbon–carbon double bond C(8)–C(10) (1.34 Å) and the geometry around this olefinic bond are normal.

The nickel containing compound (1a) reacts readily with hfb to give almost instantaneously compound (9b) as a red crystalline product. Its ^1H n.m.r. spectrum is similar to that of (9a) and its i.r. spectrum is quasi-identical to (9a). We therefore propose a *cis* configuration for this compound.

The symmetrical bicyclic compound (3) reacts slowly at a

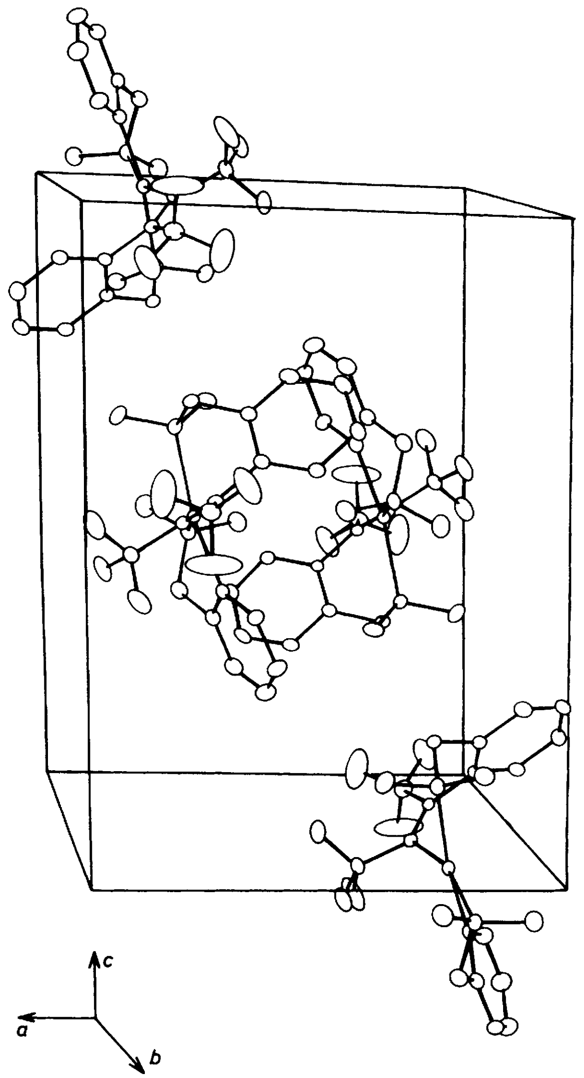
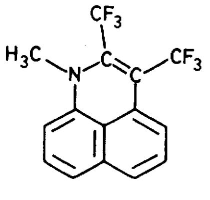


Figure 2. Molecular packing of (9a) within the unit cell



higher temperature (70 °C) with hfb in a CH_2Cl_2 solution. After 3 d, only metallic palladium is obtained together with an organic product (shown above) which has been fully characterized previously in our laboratory.[2]

Unsymmetrical bicyclic compounds (4)—(7). If compound (4) is treated with an excess of hfb at room temperature after *ca.* 8 h the pale yellow compound (10) is formed. Another isomeric form (11) is obtained if (10) is left in CH_2Cl_2 for only 1 d. The spectroscopic and analytical data for complexes (10) and (11) are of the same type as those of (8) and (9a) and therefore (10) and (11) are the *trans* and *cis* isomers respectively. The metal–carbon bond of (4) which has reacted is probably that which is present in the palladated dmba metallocycle since we have shown that once the palladated dmna moiety reacts with hfb it readily gives the organic heterocycle

Table 1. Selected bond lengths (Å) and angles (°) for (9a)

Pd–N(1)	2.231(3)	N(1)–C(20)	1.480(4)	C(7)–C(8)	1.500(4)	C(9)–F(1)	1.275(4)
Pd–N(2)	2.223(3)	N(2)–C(12)	1.502(4)	C(8)–C(9)	1.503(4)	C(9)–F(2)	1.293(4)
Pd–C(10)	2.002(3)	N(2)–C(21)	1.472(4)	C(8)–C(10)	1.339(4)	C(9)–F(3)	1.286(4)
Pd–C(14)	2.003(3)	N(2)–C(22)	1.477(5)	C(10)–C(11)	1.504(4)	C(11)–F(4)	1.332(4)
N(1)–C(1)	1.501(4)	C(1)–C(2)	1.505(4)	C(12)–C(13)	1.484(5)	C(11)–F(5)	1.316(4)
N(1)–C(19)	1.486(4)	C(2)–C(7)	1.402(4)	C(13)–C(14)	1.404(4)	C(11)–F(6)	1.334(4)

N(1)–Pd–N(2)	100.97(0.9)	Pd–C(14)–C(13)	113.39(0.23)	C(7)–C(8)–C(10)	120.64(0.26)
N(1)–Pd–C(10)	91.75(0.10)	Pd–C(14)–C(15)	128.90(0.25)	C(8)–C(9)–F(1)	113.33(0.29)
N(1)–Pd–C(14)	170.59(0.10)	Pd–N(2)–C(12)	100.76(0.19)	C(8)–C(9)–F(2)	116.06(0.28)
N(2)–Pd–C(10)	161.39(0.10)	Pd–N(2)–C(21)	114.40(0.21)	C(8)–C(9)–F(3)	115.04(0.31)
N(2)–Pd–C(14)	81.62(0.11)	Pd–N(2)–C(22)	115.68(0.24)	C(8)–C(10)–C(11)	122.04(0.27)
C(10)–Pd–C(14)	88.02(0.12)	N(1)–C(1)–C(2)	115.08(0.25)	C(10)–C(11)–F(4)	114.06(0.26)
Pd–N(1)–C(1)	110.50(0.18)	C(1)–C(2)–C(3)	119.91(0.29)	C(10)–C(11)–F(5)	115.48(0.28)
Pd–N(1)–C(19)	112.26(0.22)	C(1)–C(2)–C(7)	121.78(0.27)	C(10)–C(11)–F(6)	112.56(0.27)
Pd–N(1)–C(20)	109.42(0.21)	C(2)–C(7)–C(8)	119.66(0.26)	N(2)–C(12)–C(13)	110.42(0.26)
Pd–C(10)–C(8)	126.25(0.21)	C(6)–C(7)–C(8)	120.69(0.26)	C(12)–C(13)–C(14)	116.19(0.28)
Pd–C(10)–C(11)	111.70(0.21)	C(7)–C(8)–C(9)	113.98(0.25)	C(12)–C(13)–C(18)	123.09(0.32)

Table 2. Selected bonds lengths (Å) and angles (°) for (12)

Pd–N(1)	2.215(8)	C(1)–C(2)	1.439(16)	C(21)–C(22)	1.480(16)	C(11)–F(5)	1.292(13)
Pd–N(2)	2.119(8)	C(2)–C(7)	1.472(15)	C(22)–C(23)	1.478(18)	C(11)–F(6)	1.345(13)
Pd–C(10)	2.016(9)	C(7)–C(8)	1.463(14)	C(22)–C(24)	1.307(14)	C(23)–F(10)	1.258(16)
Pd–C(24)	2.004(10)	C(8)–C(9)	1.511(15)	C(24)–C(25)	1.499(15)	C(23)–F(11)	1.361(18)
N(1)–C(1)	1.484(13)	C(8)–C(10)	1.408(15)	C(9)–F(1)	1.138(15)	C(23)–F(12)	1.211(16)
N(1)–C(26)	1.458(12)	C(10)–C(11)	1.450(14)	C(9)–F(2)	1.128(15)	C(25)–F(7)	1.311(14)
N(1)–C(27)	1.457(14)	C(20)–C(19)	1.405(16)	C(9)–F(3)	1.381(22)	C(25)–F(8)	1.336(13)
N(2)–C(12)	1.363(14)	C(19)–C(21)	1.573(18)	C(11)–F(4)	1.330(13)	C(25)–F(9)	1.319(12)
N(2)–C(20)	1.321(13)						

N(1)–Pd–N(2)	94.82(0.30)	Pd–C(24)–C(25)	117.80(0.81)	C(8)–C(9)–F(1)	117.67(1.20)
N(1)–Pd–C(10)	90.31(0.36)	Pd–C(24)–C(22)	115.99(0.82)	C(8)–C(9)–F(2)	126.82(1.36)
N(1)–Pd–C(24)	170.02(0.38)	N(1)–C(1)–C(2)	113.36(0.90)	C(8)–C(9)–F(3)	102.52(1.58)
N(2)–Pd–C(24)	86.94(0.35)	C(1)–C(2)–C(7)	121.94(0.98)	C(10)–C(11)–F(4)	110.69(93)
N(2)–Pd–C(10)	172.02(0.39)	C(2)–C(7)–C(8)	117.62(0.99)	C(10)–C(11)–F(5)	116.74(1.07)
C(10)–Pd–C(24)	89.06(0.40)	C(7)–C(8)–C(10)	118.76(0.82)	C(10)–C(11)–F(6)	114.20(1.00)
Pd–N(1)–C(1)	108.49(0.63)	C(7)–C(8)–C(9)	119.71(0.97)	C(24)–C(25)–F(7)	115.40(0.91)
Pd–N(1)–C(26)	116.91(0.73)	N(2)–C(20)–C(19)	122.33(1.01)	C(24)–C(25)–F(8)	111.11(1.04)
Pd–N(1)–C(27)	107.89(0.62)	C(20)–C(19)–C(21)	122.23(0.95)	C(24)–C(25)–F(9)	116.67(1.11)
Pd–C(10)–C(11)	121.60(0.86)	C(19)–C(21)–C(22)	114.79(0.89)	C(22)–C(23)–F(10)	118.35(1.38)
Pd–C(10)–C(8)	115.04(0.70)	C(21)–C(22)–C(24)	120.42(1.00)	C(22)–C(23)–F(11)	108.59(1.47)
Pd–N(2)–C(12)	109.24(0.70)	C(21)–C(22)–C(23)	115.26(1.15)	C(22)–C(23)–F(12)	118.65(1.28)
Pd–N(2)–C(20)	130.08(0.77)	C(22)–C(24)–C(25)	125.82(1.07)		

mentioned above. Under more severe conditions (higher temperature, longer reaction time) the above organic heterocycle is also obtained in this reaction together with decomposition products.

It was not possible to isolate any identifiable organometallic products from the reaction of (5) or (6) with hfb. However, compound (7) affords under similar conditions a product which can be described as a mixture of two isomers according to its ^{1}H n.m.r. spectrum. One of these isomers disappears after 2 d in solution leaving a solution of pure compound (12) which can then be obtained as yellow crystals. From the analysis it appears that two acetylenes have reacted with compound (7) affording a rather unusual metallobicyclic molecule with two seven-membered rings, attached to the same metal. Compound (12) has been fully characterized by n.m.r. and by an *X*-ray diffraction study.

The molecular structure of (12) is shown in Figure 3 which also indicates the crystallographic numbering system. The molecular packing in the unit cell is given in Figure 4. Interatomic distances and angles, fractional co-ordinates, least-square planes, and crystal data are given in Tables 2 and 5—7 respectively. The palladium atom is indeed surrounded by two seven-membered rings, the hfb having reacted with the two Pd–C bonds of (7). The two new Pd–C bonds are *cis* to each other and thus in this case also the *trans* isomer is the less stable one. The co-ordination plane of the palladium atom seems to be less distorted than in compound (9a) (see plane 1, Table 6). The Pd–C and Pd–N bond lengths are close to those found for (9a). The seven-membered ring containing the dmba ligand has a similar geometry to (9a). Note however that the dihedral angle between the two planes containing the seven atoms used to describe the ring is now 70.1°. This lower value could reflect the increased crowding around palladium in (12). The two best planes 6 and 7 (Table 6) give a good description of the second seven-membered ring: plane 6 contains the olefinic moiety, while plane 7 contains the four atoms of the 8Me-quin ligand. The dihedral angle between these planes is 112.3°. As a consequence of the increase in ring size from five to seven atoms, the plane of the quinoline moiety (plane 5, Table 6) now makes a dihedral angle of 112.2° (or its supplement, 67.8°) with the co-ordination plane of the palladium (plane 1, Table 6), a value which is very close to the dihedral angles found between pyridine (py) and the square plane of platinum in *cis*- and *trans*-[Pt(py)$_2$Cl$_2$].[13]

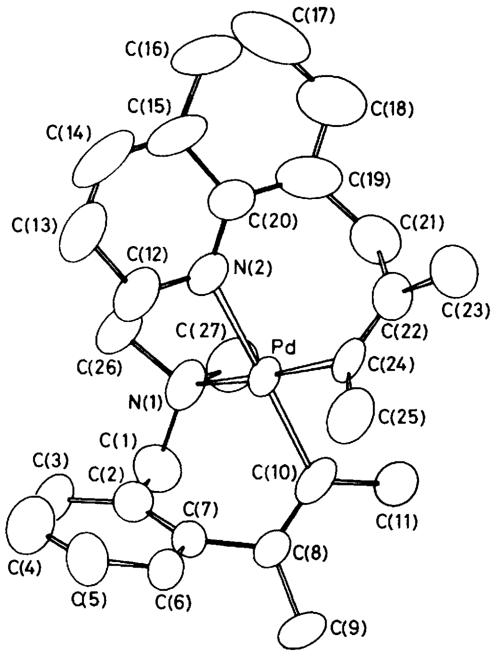


Figure 3. ORTEP drawing of compound (12). All hydrogen and fluorine atoms have been omitted for clarity

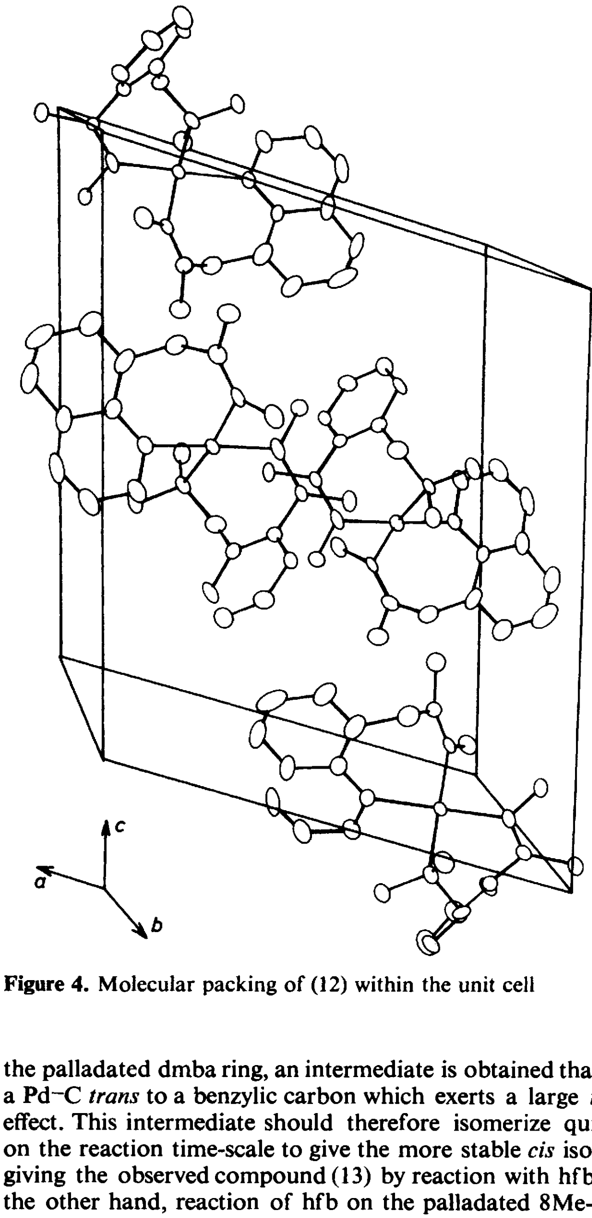


Figure 4. Molecular packing of (12) within the unit cell

Compound (7) is thus by far the most reactive of the series and we have therefore studied its reaction with $MeO_2CC{\equiv}CCO_2Me$. It gives a mixture of products of which only compound (14) has been fully characterized. The analysis reveals that only one acetylene has reacted with (7). In the ^1H n.m.r. spectrum two peaks are assigned to the methyl protons of the acetylene at 3.69 and 3.5 p.p.m. The CH_2 protons of 8Me-quin are found at similar chemical shifts to (12) or (13) whereas the two H of the CH_2 of the dmba ligand are found at chemical shifts (3.87 and 3.73 p.p.m.) which differ greatly from the values of seven-membered rings containing a dmba moiety. This last result suggests that the acetylene has reacted with the Pd–C bond of the palladated 8Me-quin ring and not with that of the palladated dmba. This time no isomerization takes place in solution.

Finally, as a conclusion, the metal–carbon bonds of the metallobicyclic compounds (1)—(7) are fairly reactive towards the insertion of acetylenes and compounds containing seven-membered rings can indeed by obtained by this way.

Starting with compounds having two Pd–C bonds *cis* to each other by reaction with acetylene we obtain first an isomer in which the two Pd–C bonds are *trans* to each other. This suggests to us reaction Scheme 1 (although others are possible).

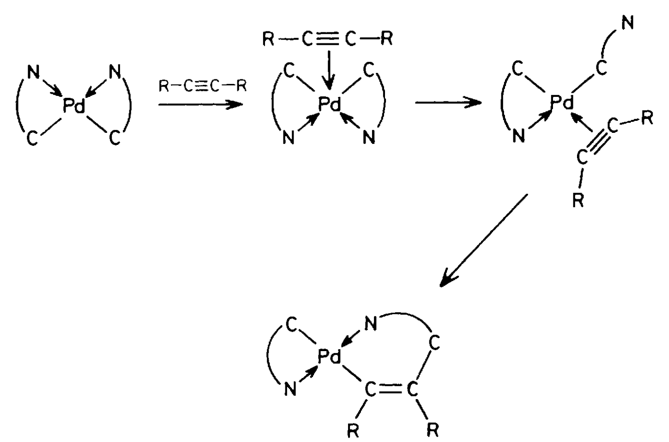
Though we did not make any kinetic measurements on this reaction we believe that the slow step of this sequence is the co-ordination of the acetylene in the co-ordination plane of the metal *trans* to a Pd–C bond after one N→Pd bond has been broken. We have shown in other cases that the reaction is indeed much faster when a vacant site is easily accessible for the acetylene in the Pd square plane (*e.g.* when a bridged chlorine or a methoxy group is bound to the metal).[10] The addition of the $\mathrm{Pd{-}\overline{C\ N}}$ moiety to the acetylene can then occur[14] to give the final product with a *trans*-C–Pd–C arrangement.

In the case of the reaction of compound (7) which bears two Pd–C bonds of different nature, the fact that a 1 : 1 mixture of *cis* and *trans* products is obtained can be explained by Scheme 2. Once the reaction is complete on the Pd–C bond of the palladated dmba ring, an intermediate is obtained that has a Pd–C *trans* to a benzylic carbon which exerts a large *trans* effect. This intermediate should therefore isomerize quickly on the reaction time-scale to give the more stable *cis* isomer, giving the observed compound (13) by reaction with hfb. On the other hand, reaction of hfb on the palladated 8Me-quin side leads to a *trans* intermediate, which is stable on the reaction time-scale. It then gives compound (12) by reaction of the acetylene with the palladated dmba ring.

Experimental

The compounds [{Pd(dmba – H)Cl}$_2$],[7] [{Pd(8Me-quin – H)-Cl}$_2$], and [M(dmba – H)$_2$] (1a)—(1c)[3] were prepared by literature methods. Lithiated dmba and dmat were obtained as published.[15] All solvents were dried and distilled under N_2 prior to use. The syntheses were performed by the Schlenk-tube techniques in an atmosphere of N_2 (or argon for the nickel compounds).

The i.r. spectra were recorded as KBr pellets with a Perkin-Elmer 398 spectrophotometer. The ^1H and $^{13}C-\{^1H\}$ spectra were recorded at 200.00 and/or 250.00 and at 50.32 and/or 62.86 MHz respectively on a Brucker SY-200 or Cameca 250 instrument. Proton and carbon chemical shifts are positive downfield relative to external $SiMe_4$. The ^{19}F n.m.r. spectra were recorded at 84.67 MHz on a Bruker WH-90 instrument, the chemical shifts being positive upfield relative to external $CFCl_3$.



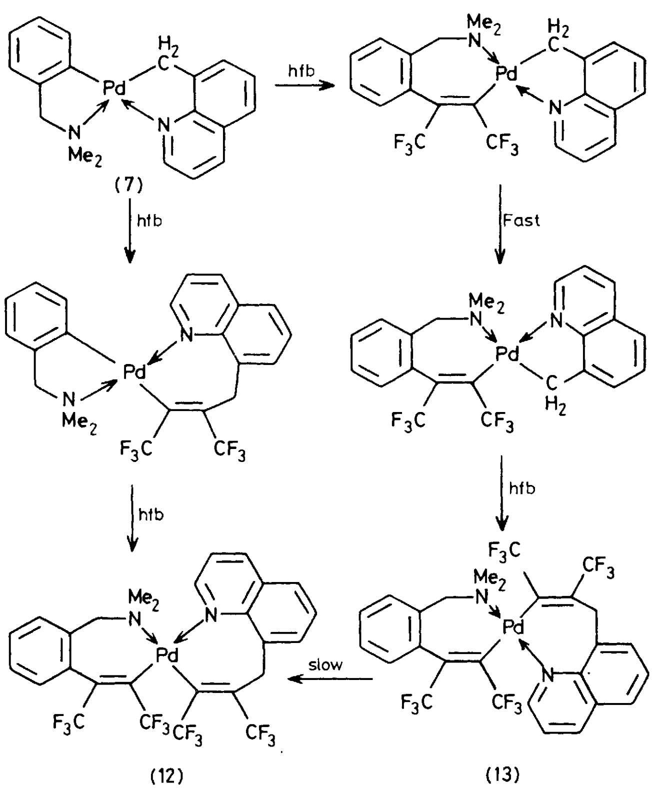
Scheme 1. R = CF_3 or CO_2Me

Elemental analyses were performed by the Service de Microanalyses du C.N.R.S.

Lithiation of NN-*Dimethyl*-1-*naphthylamine* (*dmna*).—To a solution of 5 cm^3 of dmna (5.22 g, 30.5 mmol) in diethyl ether (10 cm^3) and n-hexane (10 cm^3) was added n-butyl-lithium (20 cm^3, 1.6 mol dm^{-3} in n-hexane, 32 mmol). The mixture was stirred for 4 d at room temperature affording a white precipitate, which was filtered, washed with n-pentane (50 cm^3) and dried *in vacuo* (6.05 g, 79%). ^1H N.m.r. (C_6D_6): δ 8.37 (dd, 1 H), 7.79 (m, 2 H), 7.42 (t, 1 H), 7.20 (m, 2 H), (6 aromatic protons), 3.32 (q, 4 H, CH_2 of Et_2O), 2.28 (s br, 3 H, NCH_3), 1.78 (s br, 3 H, NCH_3), and 1.16 p.p.m. [t, 6 H, CH_3 of Et_2O, ^3J(H−H) = 7 Hz]. ^{13}C N.m.r. (C_6D_6): δ 178.3 (br, lithiated carbon), 156.2, 143.3, 136.3, 135.6, 128.1, 126.9, 125.2, 124.8, 116.0 (aromatic carbons), 65.8 (CH_2 of Et_2O), 49.5 (br, NCH_3), 45.0 (br, NCH_3), and 15.4 p.p.m. (CH_3 of Et_2O).

[Pd(dmat − H)$_2$] (2a).—A suspension of lithiated dmat (1.99 g, 14.1 mmol) in toluene (15 cm^3) was added dropwise to a solution of [$PdCl_2(SEt_2)_2$] (2.52 g, 7.1 mmol) in toluene (15 cm^3) at 0 °C. After 15 min stirring the black solution was filtered on a short column of alumina which was then washed with toluene (50 cm^3). The volume of the yellow solution thus obtained was reduced to 20 cm^3 *in vacuo*. Addition of n-hexane afforded at −20 °C brownish crystals of (2a) (0.04 g, 1.5%) (Found: C, 57.1; H, 5.9; N, 7.65. $C_{18}H_{24}N_2Pd$ requires C, 57.7; H, 6.45; N, 7.45%). ^1H N.m.r. (C_6D_6): δ 7.59—6.83 (m, 4 H, C_6H_4), 2.98 (s, 2 H, CH_2), 2.60 p.p.m. [s, 6 H, $N(CH_3)_2$].

[Pt(dmat − H)$_2$] (2b).—A solution of lithiated dmat (1.75 g, 12.4 mmol) in thf (20 cm^3) was added dropwise to a solution of *cis*-[$PtCl_2(SEt_2)_2$] (2.78 g, 6.2 mmol) in thf (35 cm^3) at room temperature. After stirring for 1 h the solvent of the black solution was removed *in vacuo*. The residue thus obtained was washed with water, then with n-hexane (30 cm^3) and dissolved in toluene (100 cm^3). This solution was filtered on a short column (5 cm) of alumina and the solvent removed *in vacuo*. The residue was dissolved in thf (20 cm^3) and addition of n-hexane afforded at −20 °C cream crystals of (2b) (1.58 g, 54%). Our spectroscopic data are in good agreement with those reported by Van Der Ploeg *et al.*[5]



Scheme 2.

[Pd(dmna − H)$_2$](3).—A solution of [{Li(dmna − H)}$_n$·$n$$Et_2O$] (2.7 g, 10.7 mmol) in toluene (30 cm^3) was added dropwise to a solution of [$PdCl_2(SEt_2)_2$] (1.91 g, 5.3 mmol) in toluene (20 cm^3) at room temperature. After stirring for 1 h the toluene of the brown solution was removed *in vacuo*. The residue was washed twice with n-pentane (15 cm^3) and dissolved in dichloromethane (40 cm^3). Addition of n-pentane gave at −20 °C compound (3) as white needles (1.32 g, 55%) (Found: C, 62.65; H, 5.4; N, 5.8. $C_{24}H_{24}N_2Pd$ requires C, 62.5; H, 5.4; N, 6.25%). ^1H N.m.r. (CD_2Cl_2): δ 7.71—7.39 (m, 6 H, aromatic protons), 3.27 p.p.m. [s, 6 H, $N(CH_3)_2$]. ^{13}C N.m.r. ($CDCl_3$): δ 155.1, 153.6, 140.8, 135.2, 133.8, 126.9, 126.6, 124.3, and 113.5 (aromatic carbons), 51.3 p.p.m. [$N(CH_3)_2$].

[Pd(dmna − H)(dmba − H)] (4).—A solution of [{Li(dmna − H)}$_n$·$n$$Et_2O$] (2.56 g, 10.2 mmol) in thf (30 cm^3) was added dropwise to a suspension of [{Pd(dmba − H)Cl}$_2$] (2.83 g, 5.1 mmol) in thf (20 cm^3). After stirring for 30 min the thf was removed *in vacuo* and the residue washed with two portions of n-pentane (30 cm^3) and then dissolved in toluene (150 cm^3). This solution was filtered and gave after addition of n-pentane at −20 °C white plates of (4) (2.0 g, 48%) (Found: C, 60.95; H, 5.85; N, 7.85. $C_{21}H_{24}N_2Pd$ requires C, 61.4; H, 5.9; N, 6.8%). ^1H N.m.r. (CD_2Cl_2): δ 7.69—6.97 (m, 10 H, aromatic protons), 3.96 (s, 2 H, CH_2−N), 3.21 [s, 6 H, $N(CH_3)_2$ of dmna], and 2.62 p.p.m. [s, 6 H, $N(CH_3)_2$ of dmba]. ^{13}C N.m.r. (CD_2Cl_2): δ 147.5, 139.1, 135.7, 133.9, 126.9, 126.8, 125.9, 124.6, 123.0, 122.2, 121.9, 114.9 (aromatic carbons), 72.6 (CH_2−N), 51.5 [$N(CH_3)_2$ of dmna], and 49.3 p.p.m. [$N(CH_3)_2$ of dmba].

[Pd(dmna − H)(8Me-quin − H)] (5).—A procedure similar to that used for the synthesis of (4) but using [{Pd(8Me-quin − H)Cl}$_2$] instead of [{Pd(dmba − H)Cl}$_2$] afforded (5) as yellow microcrystals (60%) (Found: C, 62.8; H, 5.0; N, 6.4. $C_{20}H_{20}N_2Pd$ requires C, 63.1; H, 4.8; N, 6.7%). ^1H N.m.r. (CD_2Cl_2): δ 8.93—7.32 (m, 12 H, aromatic protons), 3.38 [s, 6 H, $N(CH_3)_2$], and 3.36 p.p.m. (s, 2 H, CH_2−Pd). ^{13}C N.m.r.

(CD_2Cl_2): δ 147.7, 138.2, 131.4, 130.2, 128.1, 127.1, 126.8, 124.6, 123.2, 122.0, 121.0, 115.7 (aromatic carbons), 52.0 $[N(CH_3)_2]$, and 23.4 p.p.m. $(CH_2\text{-}Pd)$.

[Pd(dmba − H)(dmat − H)] (6).—A solution of lithiated dmat (1.05 g, 7.4 mmol) in thf (30 cm^3) was added dropwise to a suspension of [{Pd(dmba − H)Cl}$_2$] (2.04 g, 3.7 mmol) in thf (50 cm^3) at room temperature. The solution turned black rapidly and the solvent was then quickly removed *in vacuo*. The residue was washed with n-hexane (30 cm^3), dissolved in dichloromethane (50 cm^3), and filtered on a short column of alumina. The CH_2Cl_2 of the yellow solution thus obtained was removed *in vacuo* and the residue washed with hexane (20 cm^3) to give a yellow solid (1.75 g). It is in fact a 5 : 1 mixture of (6) and [Pd(dmba − H)$_2$] (1b) respectively as shown by its ^1H n.m.r. spectrum. The solubilities of these two compounds are too close to allow a better purification of compound (6). ^1H N.m.r. (CD_2Cl_2): δ 7.37—6.92 (m, 8 H, C_6H_4), 3.72 (s, 2 H, $CH_2\text{-}N$), 3.03 [s, 6 H, $N(CH_3)_2$], 2.79, (s, 2 H, $CH_2\text{-}Pd$), and 2.61 p.p.m. [s, 6 H, $N(CH_3)_2$]. ^{13}C N.m.r. (CD_2Cl_2): δ 155.0, 151.4, 148.0, 134.7, 130.7, 126.5, 125.1, 125.0, 121.6, 119.5 (aromatic carbons), 71.3 $(CH_2\text{-}N)$, 50.7 $[N(CH_3)_2]$, 49.6 $[N(CH_3)_2]$, and 21.8 p.p.m. $(CH_2\text{-}Pd)$.

[Pd(8Me-quin − H)(dmba − H)] (7).—A solution of lithiated dmba (0.79 g, 5.6 mmol) in thf (20 cm^3) was slowly added to a suspension of [{Pd(8Me-quin − H)Cl}$_2$] (1.30 g, 2.3 mmol) in thf (20 cm^3) at room temperature. After stirring for 30 min the solvent was removed *in vacuo* and the residue washed with n-pentane (15 cm^3) and diethyl ether (5 cm^3), then with water and again with n-pentane. It was then dissolved in toluene (70 cm^3) and this solution was filtered. Compound (7) was obtained by removing the toluene of this solution *in vacuo* and by washing the yellow powder thus obtained with 10 cm^3 of pentane (1.02 g, 58%). Analytically pure (7) is obtained by crystallizing it in a toluene–pentane mixture at −20 °C as yellow crystals (Found: C, 59.65; H, 5.2; N, 6.55. $C_{19}H_{20}N_2Pd$ requires C, 59.6; H, 5.25; N, 7.3%). ^1H N.m.r. $(CDCl_3)$: δ 8.76—6.94 (m, 10 H, aromatic protons), 3.84 (s, 2 H, $CH_2\text{-}N$), 3.25 (s, 2 H, $CH_2\text{-}Pd$), and 2.79 p.p.m. [s, 6 H, $N(CH_3)_2$]. ^{13}C N.m.r. (CD_2Cl_2): δ 159.0, 152.3, 151.7, 148.6, 148.0, 137.7, 135.4, 129.5, 127.8, 125.1, 122.9, 122.4, 120.9 (aromatic carbons), 71.8 $(CH_2\text{-}N)$, 49.8 $[N(CH_3)_2]$, and 21.9 p.p.m. $(CH_2\text{-}Pd)$.

Reactions of the Bicyclic Compounds with Acetylenes.—trans *Complex* (8) *and* cis *complex* (9a). Hexafluorobut-2-yne (8.4 mmol) was condensed *in vacuo* at −196 °C in a Schlenk tube containing a solution of compound (1b) (0.52 g, 1.4 mmol) in thf (40 cm^3). After stirring for 24 h at room temperature this solution was filtered and the solvent removed *in vacuo*. Washing the residue with (20 cm^3) afforded compound (8) in a pure form (0.62 g, 85%). It can be crystallized in a mixture of CH_2Cl_2–pentane at −20 °C as yellow crystals (Found: C, 49.9; H, 4.8; N, 5.35. $C_{22}H_{24}F_6N_2Pd$ requires C, 49.2; H, 4.5; N, 5.2%). ^1H N.m.r. (CD_2Cl_2): δ 7.61—6.83 (m, 8 H, C_6H_4), 4.08 and 2.91 [2 H, AB spin system, $^2J(H\text{-}H)$ = 12.5, CH_2N], 3.99 and 3.03 [2 H, AB spin system, $^2J(H\text{-}H)$ = 11.6 Hz, CH_2N], 2.94 (s, 3 H, CH_3), 2.81 (s, 3 H, CH_3), 2.44 (s, 3 H, CH_3), and 2.22 p.p.m. (s, 3 H, CH_3). ^{13}C N.m.r. (CD_2Cl_2): δ 164.5, 147.6, 140.3, 135.3, 134.7, 131.6, 128.4, 128.1, 126.8, 124.3, 123.3, and 121.3 (C_6H_4), 76.9 and 69.5 (CH_2), 53.9, 53.7, 52.2, and 50.0 p.p.m. $[N(CH_3)_2]$. ^{19}F N.m.r. $(CDCl_3)$: δ 49.25 (q, 3 F, CF_3), 58.85 p.p.m. [q, 3 F, $^5J(F\text{-}F)$ = 14.7 Hz, CF_3].

Compound (9a) can be obtained by leaving a solution of (8) in CH_2Cl_2 at room temperature for several weeks. Addition of pentane to this solution afforded (9a) as white crystals. This

Table 3. Atomic co-ordinates (× 10^4) for (9a) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pd	7 701.3(0.2)	1 179.0(0.2)	116.7(0.2)
N(1)	7 378(3)	839(3)	1 431(2)
N(2)	7 843(3)	−686(3)	−350(2)
C(1)	7 564(3)	1 963(3)	1 928(2)
C(2)	8 688(3)	2 585(3)	1 822(2)
C(3)	9 610(4)	2 374(4)	2 378(2)
C(4)	10 640(4)	2 974(4)	2 329(2)
C(5)	10 767(3)	3 785(4)	1 716(3)
C(6)	9 861(3)	4 030(3)	1 154(2)
C(7)	8 818(3)	3 443(3)	1 205(2)
C(8)	7 817(3)	3 757(3)	632(2)
C(9)	7 514(4)	5 068(4)	627(2)
C(10)	7 240(3)	2 901(3)	208(2)
C(11)	6 120(3)	3 149(4)	−258(2)
C(12)	7 573(3)	−495(4)	−1 250(3)
C(13)	8 173(3)	585(4)	−1 540(2)
C(14)	8 251(3)	1 560(3)	−995(2)
C(15)	8 800(4)	2 582(4)	−1 254(2)
C(16)	9 247(4)	2 651(4)	−2 018(3)
C(17)	9 164(4)	1 694(5)	−2 543(3)
C(18)	8 629(4)	658(4)	−2 308(2)
C(19)	6 186(4)	439(4)	1 543(3)
C(20)	8 179(4)	−91(4)	1 762(3)
C(21)	8 997(4)	−1 208(4)	−239(3)
C(22)	6 991(4)	−1 545(4)	−64(3)
F(1)	7 495(5)	5 538(3)	−86(2)
F(2)	8 166(3)	5 753(2)	1 089(2)
F(3)	6 527(3)	5 316(3)	893(3)
F(4)	5 631(2)	2 181(2)	−604(2)
F(5)	6 166(3)	3 918(3)	−867(2)
F(6)	5 323(2)	3 559(3)	225(2)

Table 4. Least-squares planes for compound (9a) and distances (Å) of atoms from planes in square brackets

Plane 1: Pd, C(14), N(2), C(10), N(1)

$$-0.9479X - 0.1043Y - 0.3010Z + 8.6922 = 0$$

[Pd −0.037(1), C(14) −0.240(3), N(2) 0.211(3), C(10) 0.238(3), N(1) −0.171(3)]

Plane 2: Pd, C(8), C(10), C(7)

$$0.6311X + 0.2088Y - 0.7471Z - 5.7992 = 0$$

[Pd 0.016(1), C(8) 0.044(3), C(10) −0.041(3), C(7) −0.019(3)]

Plane 3: Pd, N(1), C(10)

$$-0.9336X - 0.2464Y - 0.2600Z + 8.7796 = 0$$

[Pd 0.000(1), N(1) 0.000(3), C(10) 0.000(3)]

Plane 4: C(1), C(2), C(7), C(8)

$$0.2959X - 0.7217Y - 0.6258Z + 0.9759 = 0$$

[C(1) 0.000(4), C(2) 0.000(4), C(7) 0.000(3), C(8) 0.000(3)]

Plane 5: C(2), C(3), C(4), C(5), C(6), C(7)

$$0.3522X - 0.7207Y - 0.5971Z + 0.3336 = 0$$

[C(2) 0.008(4), C(3) −0.001(4), C(4) −0.009(4), C(5) 0.008(4), C(6) 0.001(4), C(7) 0.007(3)]

Plane 6: Pd, N(2), C(13), C(14), C(12) *

$$-0.9596X + 0.0662Y - 0.2735Z + 8.6796 = 0$$

[Pd 0.074(1), N(2) −0.055(3), C(13) 0.096(4), C(14) −0.115(3), C(12) * 0.586(4)]

Dihedral angles (°) between planes:

1—2	113.3	4—5	3.6
1—6	9.9	3—4	86.3
1—4	91.0		

* This atom was not used in defining the plane.

Table 5. Atomic co-ordinates ($\times 10^4$) for (12) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pd	2 452(0.6)	−2 413.9(0.7)	−3 930(5)
N(1)	2 896(8)	−1 103(9)	546(6)
N(2)	3 924(7)	−3 066(9)	−122(6)
C(1)	2 180(10)	−1 100(10)	1 040(8)
C(2)	1 961(9)	−2 160(10)	1 285(8)
C(3)	2 510(10)	−2 600(20)	2 059(8)
C(4)	2 358(12)	−3 730(10)	2 260(10)
C(5)	1 613(12)	−4 380(10)	1 704(9)
C(6)	995(10)	−3 840(20)	972(9)
C(7)	1 175(8)	−2 850(10)	731(7)
C(8)	538(8)	−2 370(10)	−45(7)
C(9)	−551(9)	−2 110(10)	−141(9)
C(10)	992(9)	−2 010(10)	−635(8)
C(11)	436(10)	−1 403(8)	58(8)
C(12)	4 165(11)	−3 600(10)	622(9)
C(13)	5 187(11)	−4 070(10)	980(11)
C(14)	5 856(11)	−3 970(10)	594(12)
C(15)	5 635(10)	−3 430(20)	−174(11)
C(16)	6 319(11)	−3 250(20)	−660(13)
C(17)	6 085(14)	−2 860(20)	−1 335(11)
C(18)	5 003(12)	−2 500(20)	−1 772(11)
C(19)	4 319(10)	−2 600(10)	−1 360(9)
C(20)	4 584(9)	−2 990(10)	−538(8)
C(21)	3 204(11)	−229(10)	−1 866(8)
C(22)	2 467(10)	−3 180(10)	−1 971(8)
C(23)	2 317(12)	−3 850(20)	−2 728(10)
C(24)	2 062(8)	−3 400(10)	−1 386(7)
C(25)	1 436(10)	−4 380(10)	−1 350(9)
C(26)	3 930(10)	−1 120(10)	1 099(10)
C(27)	2 811(11)	−8(1)	103(10)
F(1)	−750(7)	−1 891(17)	443(7)
F(2)	−1 133(7)	−1 798(15)	−718(7)
F(3)	−989(9)	−3 128(15)	−227(15)
F(4)	1 060(7)	−1 107(8)	−1 802(6)
F(5)	−254(7)	−2 030(8)	−1 929(5)
F(6)	−32(8)	−555(8)	−1 294(7)
F(7)	1 457(8)	−4 681(7)	−601(6)
F(8)	469(7)	−4 212(11)	−1 779(9)
F(9)	1 693(7)	−5 292(8)	−1 634(7)
F(10)	1 452(9)	−4 224(12)	−3 082(6)
F(11)	2 483(14)	−3 220(14)	−3 334(7)
F(12)	2 896(8)	−4 590(10)	−2 708(7)

Table 6. Least-squares planes for compound (12) and distances (Å) of atoms from planes in square brackets

Plane 1: Pd, N(1), N(2), C(10), C(24)

$$0.3702X + 0.6717Y - 0.6417Z + 0.2283 = 0$$

[Pd −0.026(1), N(1) 0.142(11), N(2) 0.137(11), C(10) 0.148(13), C(24) 0.169(13)]

Plane 2: Pd, N(1), C(10)

$$0.3102X + 0.6347Y - 0.7078Z + 0.3196 = 0$$

[Pd 0.000(1), N(1) 0.000(10), C(10) 0.000(13)]

Plane 3: C(1), C(2), C(7), C(8)

$$0.8112X - 0.3677Y - 0.4547Z - 1.7531 = 0$$

[C(1) 0.016(15), C(2) −0.031(13), C(7) 0.030(12), C(8) −0.015(12)]

Plane 4: C(2), C(3), C(4), C(5), C(6), C(7)

$$0.8341X - 0.3289Y - 0.429Z - 1.6638 = 0$$

[C(2) 0.026(13), C(3) −0.041(16), C(4) 0.009(17), C(5) 0.040(17), C(6) −0.059(16), C(7) 0.025(12)]

Plane 5: N(2), C(12), C(13), C(14), C(15), C(20), C(19), C(18), C(17), C(16)

$$-0.1538X - 0.8891Y - 0.4312Z - 2.6810 = 0$$

[N(2) −0.085(11), C(12) −0.010(14), C(13) 0.073(16), C(14) 0.052(18), C(15) −0.025(19), C(20) −0.058(14), C(19) 0.078(14), C(18) 0.071(19), C(17) −0.027(23), C(16) −0.069(25)]

Plane 6: Pd, C(24), C(22), C(21)

$$-0.6443X + 0.6190Y - 0.4492Z + 3.9012 = 0$$

[Pd 0.005(1), C(24) −0.012(13), C(22) 0.014(14), C(21) −0.007(14)]

Plane 7: N(2), C(19), C(20), C(21), Pd *

$$-0.0899X - 0.9420Y - 0.3234Z - 3.1365 = 0$$

[N(2) −0.007(11), C(19) −0.014(14), C(20) 0.015(15), C(21) 0.006(13), Pd −0.453]

Dihedral angles (°) *between planes*

1—2	5.5	2—3	70.1
1—3	69.8	2—6	59.3
1—4	68.2	3—4	2.7
1—5	112.2	6—7	112.3

* This atom was not used in defining the plane.

reaction can be accelerated in the presence of carbon monoxide by the following procedure. A solution of (8) (0.21 g, 0.4 mmol) in thf (10 cm^3) was stirred in an atmosphere of CO. Metallic palladium (24 mg, 0.23 mmol) was formed. After stirring for 24 h the solution was filtered and the thf removed *in vacuo*. The residue was washed with pentane affording (9a) in a pure form (0.09 g, 40%) (Found: C, 49.1; H, 4.55; N, 5.3. $C_{22}H_{24}F_6N_2Pd$ requires C, 49.2; H, 4.5; N, 5.2%). ^{1}H N.m.r. (CD_2Cl_2): δ 7.60—6.75 (m, 8 H, C_6H_4), 4.34 and 3.0 [2 H, AB spin system, ^2J(H–H) = 12.9, CH_2], 3.99 and 2.98 [2 H, AB spin system, ^2J(H–H) = 11.8 Hz, CH_2], 2.64 (s, 3 H, CH_3), 2.63 (s, 3 H, CH_3), 2.58 (s, 3 H, CH_3), and 1.89 p.p.m. (s, 3 H, CH_3). This compound was too insoluble to give a good ^{13}C n.m.r. spectrum. ^{19}F N.m.r.: δ 49.8 (q, 3 F, CF_3) and 58.4 p.p.m. [q, 3 F, ^5J(H–H) = 14 Hz, CF_3].

cis *Complex* (9b). Hexafluorobut-2-yne (0.7 mmol) was condensed at −196 °C in a Schlenk tube containing a solution of [Ni(dmba − H)$_2$] (1a) (0.078 g, 0.24 mmol) in thf (20 cm^3). The solution was warmed up to 25 °C and turned immediately red. Addition of pentane afforded at −20 °C orange microcrystals (0.050 g, 42%) (Found: C, 53.3; H, 4.75; N, 5.5. $C_{22}H_{24}F_6N_2Ni$ requires C, 54.0; H, 4.95; N, 5.75%). ^{1}H N.m.r. (CD_2Cl_2): δ 7.80—6.60 (m, 8 H, C_6H_4), 4.85 and 2.93 [2 H, AB spin system, ^2J(H–H) = 13, CH_2], 3.53 and 2.80 [2 H, AB spin system, ^2J(H–H) = 12 Hz, CH_2], 2.65 (s, 3 H, CH_3), 2.51 (s, 3 H, CH_3), 2.40 (s, 3 H, CH_3), and 1.75 p.p.m. (s, 3 H, CH_3). Compound (9b) was to insoluble to give good ^{13}C and ^{19}F n.m.r. spectra.

trans *Complex* (10) *and* cis *complex* (11). Hexafluorobut-2-yne (4.2 mmol) was condensed in a solution of (4) (0.29 g, 0.7 mmol) in toluene (30 cm^3). After stirring for 8 h at room temperature the solvent was removed *in vacuo*. The residue was washed twice with pentane (10 cm^3) and dissolved in CH_2Cl_2. Addition of pentane afforded (10) as pale yellow crystals (0.25 g, 63%). Complex (10) isomerizes quickly in a CH_2Cl_2 solution to give (11) after 1 d. It crystallizes in a CH_2Cl–pentane solution as light yellow crystals (Found: C, 53.2; H, 4.45; N, 5.4. $C_{25}H_{24}F_6N_2Pd$ requires C, 52.4; H, 4.2; N, 4.9%). ^{1}H N.m.r. ($CDCl_3$): compound (10), δ 7.62—7.12 (m, 10 H, aromatic protons), 4.08 and 3.03 [2 H, AB spin system, ^2J(H–H) = 11.5 Hz, CH_2], 3.08 (s, 3 H, CH_3), 3.05 (s, 3 H, CH_3), 2.97 (s, 3 H, CH_3) and 2.88 p.p.m. (s, 3 H, CH_3); compound (11), δ 7.58—7.18 (m, 10 H, aromatic protons), 4.11 and 3.06 [2 H, AB spin system, ^2J(H–H) = 12 Hz], 3.27 (s, 3 H, CH_3), 2.71 (s, 6 H, CH_3), and 2.64 p.p.m. (s, 3 H, CH_3).

Table 7. Summary of crystal data and intensity collection of (9a) and (12)

Compound	(9a)	(12)
Formula	$C_{22}H_{24}F_6N_2Pd$	$C_{27}H_{20}F_{12}N_2Pd$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_{1/n}$	$P2_{1/n}$
a/Å	11.705(2)	13.948(8)
b/Å	11.146(2)	12.338(7)
c/Å	16.317(5)	16.868(6)
β/°	93.16(2)	107.89(4)
U/Å^3	2 125.5	2 762.5
M	547.9	706.8
Z	4	4
D_c/g cm^{-3}	1.712	1.699
Crystal dimensions/mm	0.18 × 0.18 × 0.27	0.09 × 0.18 × 0.36
λ(Mo-K_α)/Å	0.709 26	0.709 26
μ/cm^{-1}	9.298	7.601
F(000)	1 124	1 400
Scan range/°	$1 + 0.35 \tan \theta$	$1 + 0.35 \tan \theta$
2θ limits/°	4—50	4—52
Reflections, total	4 077	5 830
Reflections, $I/\sigma(I) > 3.0$	3 288	2 228
$R = \Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$	0.046	0.061
$R' = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w F_o^2]^{\frac{1}{2}}$	0.044	0.088
Standard error in an observation of unit weight	1.035 e	1.95 e
p Factor	0.065	0.07

^{19}F N.m.r. ($CDCl_3$): compound (11), δ 48.15 (q, 3 F, CF_3), 59.10 p.p.m. [q, 3 F, ^5J(F–F) = 14 Hz, CF_3].

cis *Complex* (12) *and* trans *complex* (13). Hexafluorobut-2-yne (4.3 mmol) was condensed in a solution of compound (7) (0.324 g, 0.85 mmol) in toluene (25 cm^3). After stirring for 18 h at room temperature the solvent of the yellow-orange solution was removed *in vacuo*. The residue was washed with pentane (20 cm^3). It consists of a 1 : 1 mixture of (12) and (13). Complex (13) however is isomerized to (12) after 2 d in a CH_2Cl_2 solution. Complex (12) is then crystallized in a toluene–pentane mixture at −20 °C as pale yellow crystals (0.06 g, 10%) (Found: C, 45.25; H, 2.85; N, 4.6. $C_{27}H_{20}F_{12}N_2Pd$ requires C, 45.9; H, 2.85; N, 3.95%). ^{1}H N.m.r. ($CDCl_3$): compound (12), δ 8.21—7.19 (m, 10 H, aromatic protons), 6.76 and 4.22 [2 H, AB spin system, ^2J(H–H) = 14, CH_2 of 8Me-quin], 3.99 and 2.90 [2 H, AB spin system, ^2J(H–H) = 12 Hz, CH_2–N], 2.70 (s, 3 H, CH_3), and 1.67 p.p.m. (s, 3 H, CH_3); compound (13), δ 9.33—7.16 (m, 10 H, aromatic protons), 4.45 and 3.15 [2 H, AB spin system, ^2J(H–H) = 15, CH_2 of 8Me-quin], 3.98 and 2.95 [2 H, AB spin system, ^2J(H–H) = 11.5 Hz, CH_2–N], 2.63 (s, 3 H, CH_3), and 1.66 p.p.m. (s, 3 H, CH_3). ^{13}C N.m.r. (CD_2Cl_2): compound (12), δ 152.0, 139.9, 133.8, 131.7, 129.8, 129.1, 128.9, 127.8, 127.7, and 120.9 (aromatic carbons), 63.7, 52.2, 49.0, and 41.3 p.p.m. (CH_2 and CH_3). ^{19}F N.m.r. ($CDCl_3$): compound (12), 51.9 (q, 3 F, CF_3), 54.0 (q, 3 F, CF_3), 59.2 [2 overlapping quartets, 6 F, ^5J(F–F) = 14 Hz, CF_3].

Complex (14). A solution of $MeO_2CC{\equiv}CCO_2Me$ (0.34 mg, 2.6 mmol) in thf (6 cm^3) was added dropwise to a solution of (7) (0.50 g, 1.3 mmol) in thf (35 cm^3). After stirring for 15 h the solvent was removed *in vacuo* and the yellow residue washed with two portions of pentane (10 cm^3) and with toluene (50 cm^3). Compound (14) was extracted from the residue by CH_2Cl_2 (20 cm^3). Addition of pentane to this solution gave (14) at −20 °C as white microcrystals (0.08 g, 11.5%) [Found: C, 52.0; H, 4.55; N, 4.7. $C_{25}H_{26}N_2O_4Pd{\cdot}0.8CH_2Cl_2$ requires C, 51.2; H, 4.65; N, 4.6% (0.8CH_2Cl_2 per molecule detected by ^{1}H n.m.r.)]. ^{1}H N.m.r. ($CDCl_3$): δ 9.29—6.97 (m, 10 H, aromatic protons), 6.38 and 4.45 [2 H, AB spin system, ^2J(H–H) = 13.5, CH_2 of 8Me-quin], 3.87 and 3.73 [2 H, AB spin system, ^2J(H–H) = 13 Hz, CH_2–N], 3.69 (s, 3 H, CH_3–O), 3.50 (s, 3 H, CH_3–O), 2.33 (s, 3 H, CH_3–N), and 2.19 p.p.m. (s, 3 H, CH_3–N).

Collection of X-*Ray Data and Structure Determination.*—Cell constants and other pertinent data are presented in Table 7. Intensity data were collected on a Nonius CAD 4 diffractometer. No intensity decay was observed during the data collection periods. For compound (12) it was not possible to obtain better diffracting crystals. The quality of the structure determinations are given by R and R' (Table 7) and the σ values (Tables 1 and 2). Absorption corrections were omitted in view of the low linear absorption coefficients. The molecular structures were solved from Fourier-difference syntheses following location of most of the non-hydrogen atoms with the program MULTAN.[16,17] The co-ordinates of the hydrogen atoms were computed; for compound (9a) only their contributions were introduced in the refinement with thermal parameters equal to those of the carbon atoms to which they were bonded. In the case of compound (12) the co-ordinated hydrogen atoms were not refined. All calculations were performed on a PDP 11/60 computer with the computation programs of Frenz.[18]

Acknowledgements

We thank the C.N.R.S. for support and Professor J. Dehand for his interest throughout.

References

1 Part 6, M. Pfeffer, G. Le Borgne, and D. Grandjean, *Inorg. Chem.*, 1981, **20**, 4426.

2 A. Bahsoun, J. Dehand, M. Pfeffer, M. Zinsius, S. E. Bouaoud, and G. Le Borgne, *J. Chem. Soc., Dalton Trans.*, 1979, 547 and refs. therein.

3 G. Longoni, P. Fantucci, P. Chini, and F. Canziani, *J. Organomet. Chem.*, 1972, **39**, 413.

4 S. Trofimenko, *Inorg. Chem.*, 1973, **12**, 1215; H. P. Abicht and K. Issleib, *J. Organomet. Chem.*, 1978, **149**, 209; 1980, **185**, 265.

5 A. F. M. J. Van Der Ploeg, G. Van Koten, K. Vrieze, and A. L. Spek, *Inorg. Chem.*, 1982, **21**, 2014.

6 J. T. B. H. Jastrzebski, G. Van Koten, M. Konijn, and C. H. Stam, *J. Am. Chem. Soc.*, 1982, **104**, 5490.

7 A. C. Cope and E. C. Friedrich, *J. Am. Chem. Soc.*, 1968, **90**, 909.

8 A. J. Deeming and I. P. Rothwell, *J. Organomet. Chem.*, 1981, **205**, 117.

9 G. Longoni, P. Chini, F. Canziani, and P. Fantucci, *Gazz. Chim. Ital.*, 1974, **104**, 249.

10 A. Mauro, H. Ossor, M. Pfeffer, J. R. Lechat, and R. H. A. Santo, *J. Organomet. Chem.*, in the press.

11 N. M. Boag, M. Green, D. M. Grove, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 2170.

12 G. Van Koten, J. T. B. H. Jastrzebski, J. G. Noltes, W. M. G. F. Pontenagel, J. Kroon, and A. L. Spek, *J. Am. Chem. Soc.*, 1978, **100**, 5021.

13 P. Colamarino and P. L. Orioli, *J. Chem. Soc., Dalton Trans.*, 1975, 1656.

14 R. F. Heck, ' Organotransition Metal Chemistry, a Mechanistic Approach,' Academic Press, London, 1974, p. 170.

15 L. E. Manzer, *J. Am. Chem. Soc.*, 1978, **100**, 8068.

16 G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, 1971, **27**, 368.

17 P. Main, *Acta Crystallogr., Sect. A*, 1978, **34**, 31.

18 B. A. Frenz, ' Computing in Crystallography,' eds. H. Schenk, R. Olthof-Hazelkamp, H. Van Konigsveld, and G. C. Bassi, Delf University Press, Holland, 1978, pp. 64—71.

Received 18*th October* 1982; *Paper* 2/1779