Reactivity of Cyclopalladated Complexes. Part 5.[1] Insertion Reactions of Diphenylacetylene, 1-Phenylprop-1-yne, and Hexafluorobut-2-yne with Cyclopalladated Compounds. Crystal and Molecular Structure of Chloro{3—4-η-4-[(2-dimethylaminomethyl)phenyl]-1,4-dimethyl-2,3-diphenylbuta-1,3-dienyl-*C*¹*N*}palladium(II) and Bromo{3—4-η-4-[(2-dimethylaminomethyl)phenyl]-2,4-dimethyl-1,3-diphenylbuta-1,3-dienyl-*C*¹*N*}palladium(II)

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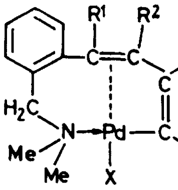
Reactions between disubstituted alkynes RC_2R' (R = R' = Ph and R = Me, R' = Ph) and $[\{Pd(dmba)X\}_2]$ (dmba = *NN*-dimethylbenzylamine, X = Cl or Br) afford bis-insertion products $[Pd\{(RC{=}CR')_2C_6H_4CH_2NMe_2\}X]$ in high yield. With MeC_2Ph two isomers have been isolated, ($1b_\alpha$) and ($1b_\beta$). In order to establish their molecular structures, a single-crystal *X*-ray diffraction study has been made on the chloro-derivative of ($1b_\beta$) and the bromo-derivative of ($1b_\alpha$). Crystals of ($1b_\alpha$; X = Br) are monoclinic, space group $P2_1/c$, $Z = 4$, with $a = 15.362(13)$, $b = 12.368(5)$, $c = 14.886(11)$ Å, and $\beta = 94.86(13)°$. The structure has been refined to *R* 0.078 (*R'* 0.105) for 2 529 independent reflections; the two acetylenes inserted into the Pd–C bond have a head-to-tail arrangement, the Pd being σ-bonded to a carbon bearing a phenyl group. Crystals of ($1b_\beta$; X = Cl) are monoclinic, space group $P2_1$, $Z = 2$, with $a = 8.227(6)$, $b = 16.059(33)$, $c = 8.923(9)$ Å, and $\beta = 99.30(12)°$. The structure has been refined to *R* 0.074 (*R'* 0.065) for 2 077 independent reflections. The molecule shows a tail-to-tail arrangement for the two inserted acetylenes, the carbon σ-bonded to the palladium bearing a methyl group. The corresponding reaction with the 8-methylquinoline palladated dimer affords a benzenoid trimer *via* a bis-insertion analogue which was isolated for R = R' = Ph. Hexafluorobut-2-yne (hfb) reacts with the above palladated dimers and those formed from benzo[*h*]quinoline and *NN*-dimethyl-1-naphthylamine to give novel halide-bridged binuclear complexes with seven-membered rings. They are formed by formal insertion of one hfb unit into the Pd–C σ bond. With the naphthylamine dimer only an organic compound was isolated. The novel dimeric complexes easily afford monomeric derivatives by bridge-splitting reactions with pyridine or PPh_3.

CYCLOMETALLATED compounds formed with appropriate stabilizing ligands show some interesting properties in organic synthesis;[2,3] thus reactions of unsaturated organic compounds with such transition-metal complexes often take place easily due to the lability of the metal–carbon σ bond. Insertion of two molecules of disubstituted alkyne into the M–C σ bond of four-membered metallacycles[4,5] (M = Rh or Ru) affords stable products; it has been shown that hexafluorobut-2-yne (hfb) inserts quite easily into the palladium–allyl bond.[6] Recently, Stone and his co-workers[7] reported the formation of substituted quinolin-2-ones *via* an isolable η-acryloyl complex of cobalt from the reaction of hfb and tricarbonyl(phenylazophenyl-2*C*,*N*)cobalt, the organometallic intermediate being formed by insertion of the alkyne and one carbonyl into the Co–C bond. Thompson and Heck[8] and other workers[9] have shown that ortho-palladation products of α-aryl nitrogen derivatives react with carbon monoxide, even under mild conditions, to give unusual heterocyclic compounds.[3] Only these organic products, not the proposed organometallic intermediate, have been isolated. The reaction of an azobenzene cyclopalladated dimer with isocyanide affords the insertion product $[PdCl(CNC_6H_{11})_2\{(CNC_6H_{11})_2C_6H_4NNPh\}]$[10] in which the cyclic ring is no longer co-ordinated to the metal. However, no insertion of acetylene into the Pd–C bond of cyclopalladated complexes has been previously reported.

This paper reports: (*i*) the insertion of what is formally a four-carbon unit (two alkyne molecules) into the Pd–C σ bond of cyclometallated compounds formed from *NN*-dimethylbenzylamine (dmba),[11] $[\{Pd(dmba)X\}_2]$ {or its monomeric derivative [Pd(dmba)(py)X] (py = pyridine, X = Cl or Br)}, and from 8-methylquinoline,[12] $[\{Pd(8Me\text{-}quin)X\}_2]$, to give, with the former only stable organometallic products and with the latter a benzenoid trimer *via* an isolable organometallic intermediate; (*ii*) the insertion of a two-carbon unit (one molecule of hfb) into the Pd–C bond of the above compounds without cleavage of the Pd_2Cl_2 unit, to give novel chloride-bridged dimers of compounds containing a seven-membered metallacycle which afford monomeric derivatives by bridge splitting with neutral ligands.

RESULTS AND DISCUSSION

Reactions between Disubstituted Alkynes, RC≡CR' (R = R' = Ph *and* R = Me, R' = Ph) *and Cyclopalladated Compounds*.—When stoicheiometric amounts of either the dimer $[\{Pd(dmba)X\}_2]$ or the monomeric pyridine derivatives [Pd(dmba)(py)X] (X = Cl or Br) and diphenylacetylene were heated under reflux in methylene chloride a deep yellow solution was formed from which yellow-orange crystals were obtained in high yield. The product is formulated as a bis-insertion complex, $[Pd\{(PhC{=}CPh)_2C_6H_4CH_2NMe_2\}X]$ (1a). The i.r. spectrum showed bands at 1 620w, 1 598m, 1 590m, and 1 577w cm⁻¹ due to ν(C=C) and a strong band assigned to terminal ν(Pd–Cl) at 320 cm⁻¹; however, for the bromo-compound the analogous vibration could not be unambiguously assigned (see below). The ^{1}H n.m.r. spectrum consisted of a multiplet at δ 6.4—7.8 p.p.m. (Ph, 24 H) and sharp singlets at 2.76 and 2.70 (5 H) and 2.32 p.p.m. (3 H). The two equally intense singlets at 2.70 and 2.32 p.p.m. are assigned to inequivalent *N*-methyl groups and that at 2.76 p.p.m. corresponds to the methylene protons.



(1a) $R^1 = R^2 = R^3 = R^4 = Ph$

(1b$_\alpha$) $R^1 = R^3 = Me$, $R^2 = R^4 = Ph$

(1b$_\beta$) $R^1 = R^4 = Me$, $R^2 = R^3 = Ph$

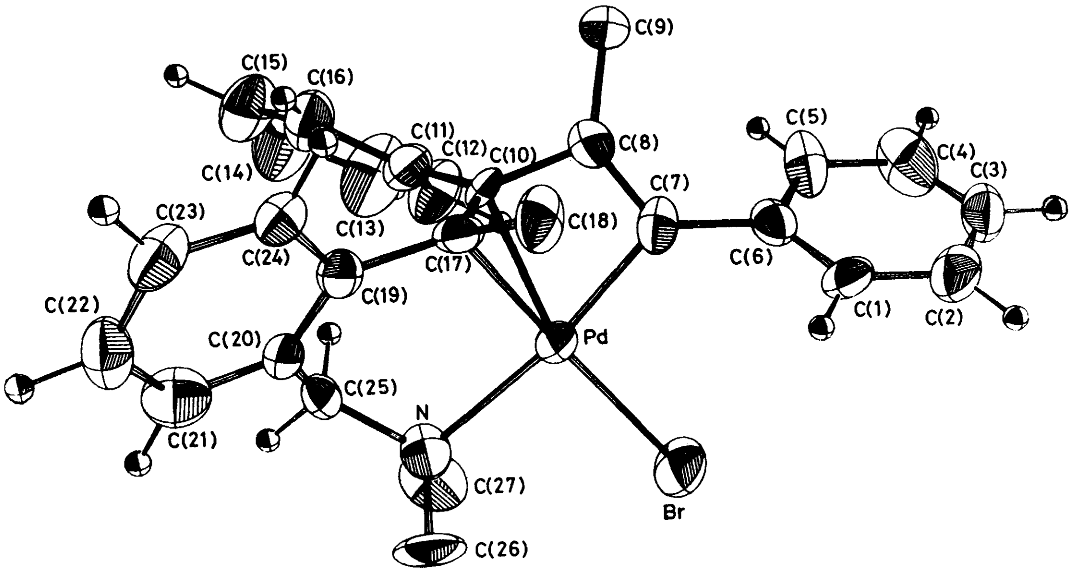


FIGURE 1 ORTEP drawing of compound (1bα; X = Br)

The corresponding reaction of either [{Pd(dmba)X}$_2$] or [Pd(dmba)(py)X] with the unsymmetric acetylene PhC$_2$Me afforded an isomeric mixture of two bis-insertion products (1b$_\alpha$) and (1b$_\beta$) which have been easily isolated. The i.r. spectra of the two isomers were nearly identical; however, differences were observed mainly in the bands due to ν(C=C) (1 594m cm^{-1} for the α form and 1 615m and 1 600m cm^{-1} for the β form) and in the 700—800 cm^{-1} region (see Experimental section). The ^{1}H n.m.r. spectrum of each form showed, in addition to aromatic proton resonances, four sharp singlets of equal intensity attributed to non-equivalent methyl groups (NMe, CMe), and signals corresponding to methylene protons which were split into an AB quartet [*J*(H–H) 14 Hz] or were broadened and ill defined from extensive overlapping of lines (δ 1.5—3.0 p.p.m., 14 H). Accordingly, assignments were made tentatively on the following considerations: (*i*) the two highest-field peaks were assigned to *C*-methyl groups, in accord with those observed for the complexes [{Pd[(CMe=CMe)$_3$Cl]Cl}$_2$] [13] and [Pd(CBu^t=CMeCMe=CBu^{t}Cl)(acac)] [14] (acac = pentane-2,4-dionate) in which one end of the olefinic chain bearing methyl substituents is linked to the metal by a Pd–C σ bond; (*ii*) the assignments of *C*-methyl groups [δ 1.60 (MeCH=) and 2.08 p.p.m. (C–MeC=C)] for (1*E*,3*Z*)-1-deuterio-2-methyl-1,3-diphenylpenta-1,3-diene [15] (PhDC=CMePhC=CHMe) can be closely related to those observed for isomer (1b$_\alpha$) (δ 1.56 and 2.16 p.p.m.); (*iii*) no drastic differences in chemical shifts should be expected for the *N*-methyl groups from one isomer to the other.

In order to establish unambiguously the molecular structure of these two isomers a single-crystal *X*-ray diffraction study was made on a bromo-derivative of one isomer and on a chloro-derivative of the other. The results of this study are given in Tables 3—8 and are illustrated in Figures 1 and 2 which also show the crystallographic numbering system. For both structures the atoms directly bonded to the palladium atoms [C(7), N, X(Cl or Br)] and A [the middle of the C(10) C(17) vector] are almost coplanar, although the deviations from these planes are rather large as shown in Tables 7 and 8. The C(10),C(17) vector is nearly perpendicular to these planes, the distances Pd–C(10) and Pd–C(17) however being significantly different. The Pd–C(7) distance is shorter in the chloro- than in the bromo-compound presumably because of the different R groups attached to these carbons. The Pd–N distances are quite large compared to other palladacyclic compounds [1,16] and this is probably due to the larger *trans* effect of a σ-bonded carbon [C(7)] than Br [1] or Co(CO)$_4$.[16] The Pd–Cl distance is normal whereas the Pd–Br one seems to be short [2.449(2); lit.,[17] 2.58 Å]. Therefore we could not assign the ν(Pd–Br) vibrations for the bis-insertion products to any i.r. absorption consistent with this short Pd–Br length. However, for these bromo-compounds, we observe an intense i.r. absorption in the range 150—156 $\mathrm{cm^{-1}}$, which is absent for the corresponding chloro-compounds. These wavenumbers are far too low for a terminal Pd–Br stretching frequency, the bromine being *trans* to an olefinic bond {ν(Pd–Br) is in the range 207—222 $\mathrm{cm^{-1}}$ for [Pd(diene)Br_2]}.[18] They are possibly a combination of different vibration modes, but they certainly contain some ν(Pd–Br) character. On the other hand, the ν(Pd–Cl) frequencies are in good agreement with those found for related compounds.[18]

In contrast to the preceding reaction of [{Pd(dmba)-X}$_2$] with acetylene, the reaction of [{Pd(8Me-quin)X}$_2$] with PhC_2Ph afforded two products separated by fractional crystallization. The first, containing 1 mol of toluene of crystallization per mol of compound, was obtained in rather poor yield. Its elemental analysis and spectroscopic features are consistent with the illustrated structure (2a), *i.e.* a bis-insertion compound for which the methylene protons appeared as a four-line AB pattern [*J*(H–H) 15 Hz] in the ^1H n.m.r. spectrum. A singlet corresponding to the methyl group of the toluene of crystallization occurs at 2.34 p.p.m. The second product was hexaphenylbenzene, identified by its elemental analysis and mass spectrum. The yield of (2a) depended on the reaction time, suggesting that this compound is an intermediate in the cyclo-oligomerization of diphenylacetylene.

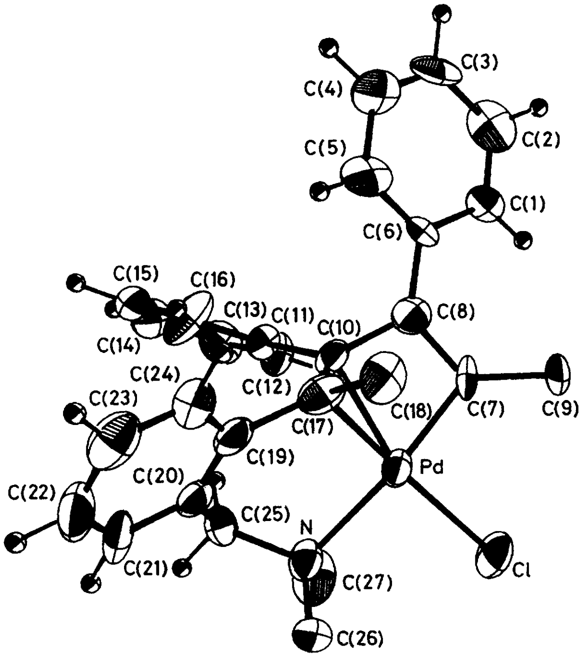
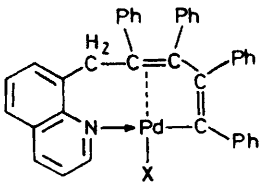


FIGURE 2 ORTEP drawing of compound (1bβ; X = Cl)



(2a)

The reaction of [{Pd(8Me-quin)X}$_2$] with PhC_2Me afforded two products analogous to (2a) and the benzenoid trimer. We could not isolate a pure metallacycle from the crude yellow mixture (very poor yield ~ 0.5%). Microanalytical data were erratic but not far from the values calculated for a bis-insertion product. The ^1H n.m.r. spectrum showed a very complex pattern in the methyl region which was not analyzable. By analogy with (2a), however, we suggest that this compound is a mixture of isomers, each of which has the same basic skeleton as that of (2a). The major product which separated as a white crystalline compound was a mixture of 1,2,4-trimethyl-3,5,6-triphenylbenzene and 1,3,5-trimethyl-2,4,6-triphenylbenzene (7 : 3, see Experimental section for ^1H n.m.r. data). The mixture was identified by elemental analysis and by its mass, and particularly ^1H n.m.r. spectra. The last spectrum unequivocally gave the proportion of each isomer formed, with the assignment according to Maitlis and his co-workers[13] who have previously separated isomers of this benzenenoid trimer.

It will be noted that only bis-insertion products were isolated when the reaction was carried out in the presence of an excess of acetylene. Attempts to produce mono-insertion complexes with PhC_2Ph or PhC_2Me, either by shortening the reaction time or by carrying out the reaction with less than a stoicheiometric amount of acetylene, failed. No reaction takes place between PhC_2Ph and cyclopalladated compounds formed from benzo[*h*]quinoline,[12] azobenzene,[19] or *NN*-dimethyl-1-naphthylamine.[11]

These reactions can be related to similar reactions of cyclometallated compounds with acetylene affording bis-insertion products, *e.g.* [Rh{(PhC=CPh)$_2C_6H_4PPh_2$}-(PPh_3)],[4] the structure of which was established by *X*-ray analysis,[20] and [Ru{($CF_3C{=}CCF_3$)$_2C_6H_4PPh_2$}(η-C_5H_5)].[5] In each of these an eight-membered ring is formed, chelating *via* M←P and M–C (M = Rh or Ru) σ bonds. In contrast, the metallacyclic structure we observe consists of a nine-membered ring (which is somewhat uncommon for palladium complexes) chelating *via* Pd←N and a Pd–C σ bond and a *trans* arrangement of the halogen atom with respect to the metal–olefin π bond.

Reactions between Hexafluorobut-2-yne and Cyclopalladated Compounds.—In order to obtain further evidence in support of insertion of acetylenes bearing electron-withdrawing substituents into the Pd–C σ bond, we have investigated the reaction between hfb and dimers formed from *NN*-dimethylbenzylamine, 8-methylquinoline, benzo[*h*]quinoline, and *NN*-dimethyl-1-naphthylamine. With the exception of the latter, the reactions proceeded to give a new type of compound for which elemental analyses and spectroscopic features indicated

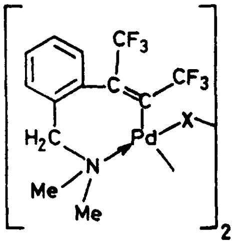
TABLE 1

Analytical data, colours, and i.r. data

Compound		X	Analysis (%)[a]					Colour	I.r. bands (cm^{-1})	
			C	H	H	F	X		ν(Pd–X)	ν(C=C)
(1a)		Cl	70.15	5.00	2.25			Deep yellow	320vs	1 620w, 1 598m, 1 590m, 1 577w
			(70.25)	(5.05)	(2.20)					
		Br	65.40	4.80	2.25			Light orange	*b*	
			(65.65)	(4.75)	(2.05)					
(1b)	α	Cl	63.9	5.50	2.65			Lemon-yellow	305vs	1 594m, 1 577w
			(63.8)	(5.50)	(2.75)					
	β	Cl	63.6	5.45	2.95		7.45	Golden-yellow	306vs	1 616m, 1 599m, 1 575w
			(63.8)	(5.50)	(2.75)		(7.00)			
	α	Br	58.55	4.90	2.65			Dark yellow	*b*	1 594m, 1 576w
			(58.65)	(5.05)	(2.55)					
	β	Br	58.5	4.95	2.60		13.6	Yellow	*b*	1 615m, 1 690m, 1 578w
			(58.65)	(5.05)	(2.55)		(14.45)			
(2a)		Cl[c]	74.25	5.55	2.15			Yellow	312s	1 629vw, 1 597m, 1583w
			(73.8)	(4.90)	(1.90)					
		Br[c]	69.25	4.65	2.00			Yellow	*b*	
			(69.55)	(4.65)	(1.80)					
(3)		Cl	35.5	2.75	3.10	26.25	8.35	Yellow	320s, 270s	1617, 1 606sh, 1 576w
			(35.6)	(2.75)	(3.20)	(26.05)	(8.10)			
		Br	32.45	2.60	3.00	23.35	16.15	Deep yellow	197s, 168s	
			(32.35)	(2.50)	(2.90)	(23.65)	(16.6)			
(4)		Cl	36.6	2.20	3.30	24.3	8.25	Pale yellow	317vs, 255ms	1 642s, 1 619vw, 1598m
			(37.7)	(1.80)	(3.15)	(25.55)	(7.95)			
		Br	34.8	2.05	3.05	23.15	15.7	Lemon-yellow	202ms, 158m	
			(34.25)	(1.65)	(2.85)	(23.25)	(16.3)		170m	
(5)		Cl	42.5	2.85	3.15			Tan	315s, 266s	1 645m, 1 622ms
			(42.35)	(1.65)	(2.90)					1 586w, 1 573m
(6)			56.8	2.75	4.35			Red		1 630s, 1 591m, 1 576s
			(56.8)	(2.85)	(4.40)					
(7a)		Cl	41.5	3.15	5.40	22.3	6.65	Pale yellow	305vs	1 608s, 1 577vw
			(41.8)	(3.30)	(5.40)	(22.05)	(6.85)			
		Br	38.7	3.10	5.00	21.0	13.9	Pale yellow	182vs	
			(38.45)	(3.05)	(5.00)	(20.3)	(14.25)			
(7b)		Cl	53.1	3.65	2.15	16.35	5.30	Pale yellow	306vs	1 611m, 1 573vw
			(53.15)	(3.85)	(2.00)	(16.3)	(5.05)			
		Br	50.1	3.45	2.10	15.0	10.55	Pale yellow	202s	
			(49.95)	(3.65)	(1.90)	(15.3)	(10.75)			
(8a)		Cl	43.0	2.40	5.25	21.85	6.90	White	309vs	1 634m, 1 609m,[d] 1 601w
			(43.45)	(2.50)	(5.35)	(21.7)	(6.75)			
(8b)		Cl	54.15	3.30	2.15	15.7	5.30	Pale yellow	312vs	1 633m, 1 600w, 1 577w
			(54.25)	(3.25)	(2.00)	(16.1)	(5.00)			

[a] Calculated values are given in parentheses. See text. [c] One molecule of toluene of crystallization per mol of compound. [d] ν(C=C) + ν(C=N) from co-ordinated py. Strong ν(C–F) between 1 080 and 1 280 cm^{-1} for all fluoro-compounds.

the presence of one hfb molecule per Pd atom in a halide-bridged binuclear complex.



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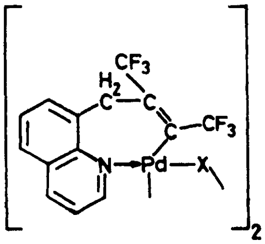

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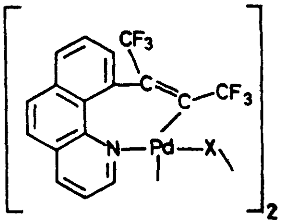
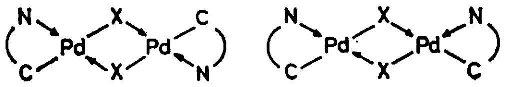


(5)

Thus [{Pd(dmba)X}$_2$] reacted over a period of several hours at 60 °C with hfb in dichloromethane to yield a yellow crystalline product [{Pd[(CF$_3$C=CCF$_3$)C$_6$H$_4$CH$_2$NMe$_2$]-X}$_2$] (3). In the i.r. spectrum several bands are assignable to ν(C=C) (see Table 1) and strong absorptions between 1 280 and 1 100 cm^{-1} are typical of ν(C–F) vibrations. In the metal–halide stretching region two strong bands, involving bridging Pd–X bonds in the binuclear Pd$_2$X$_2$ unit,[18,21,22] are observed at 320 and 270 cm^{-1} and at 197 and 168 cm^{-1} for X = Cl and Br respectively. The ^{1}H n.m.r. spectrum showed, apart from resonances indicative of phenyl protons (δ 7.2—7.6 p.p.m., 8 H), a four-line AB pattern associated with one methylene group and a complex pattern arising from the remaining protons (δ 2.3—3.0 p.p.m., 14 H): four sharp singlets of equal intensity at 2.91 and 2.75 p.p.m. and at 2.47 and 2.45 p.p.m. (Δδ 4.5 Hz) assigned to non-equivalent pairs of *N*-methyl groups in each half of the dimer, plus a broadened multiplet assigned to the second methylene group. The ^{19}F n.m.r. spectrum contained two equally intense resonances at 49.0 (q) and 59.07 (q) p.p.m. (upfield from CFCl$_3$) and two somewhat overlapped signals at 49.4 (q) and 49.6 p.p.m. (broad multiplet). The high value of the coupling constant [^5J(F^a–F^b) 13.8 Hz] suggested the presence of a *cis*-CF$_3$C=CCF$_3$ group [23] in each half of the dimer. These data strongly suggest the presence of the following two isomers in a 1 : 1 ratio: *



The corresponding reactions of the 8-methylquinoline and benzo[*h*]quinoline dimers with excess of hfb afforded the binuclear analogues (4) and (5) respectively. These products were not fully characterized due to their very low solubility in common solvents. However, the metallacyclic structures (4) and (5) depicted are supported by (*i*) elemental analysis, (*ii*) i.r. spectra containing strong absorptions typical of ν(C–F) vibrations, new bands due to ν(C=C), and two strong bands due to ν(Pd–X) stretching vibrations, (*iii*) products of bridge-splitting reactions with neutral ligands (see below). An asymmetric Pd_2Cl_2 unit in compounds (3)—(5) is suggested by a difference in ν(Pd–Cl) of 50—60 cm^{-1} in each case.[18] For palladated compounds where the bridge is symmetrical two bands in close proximity are generally observed.[24] The ^{1}H and ^{19}F n.m.r. data from product (3) are also in agreement with a low-symmetry structure. It is noteworthy that these dimeric compounds did not react either with an equivalent amount of PhC_2Ph or with an excess of hfb (*in situ*) to yield a mixed or homogeneous bis-insertion compound respectively.

TABLE 2

Hydrogen-1 and ^{19}F n.m.r. data in CD_2Cl_2 ^{a}

Compound	X	NMe^1	NMe^2	CH$_2$	^2J(CH$_2$)/Hz	CMe^1	CMe^2	H aromatic	CF$_3$(a)	CF$_3$(b)	^5J(FF)/Hz
(1a)	Cl	2.70s ^{b}	2.32s, 3 H	2.76s ^{b}				6.4—7.8m, 24 H			
(1b) α	Cl	2.97s, 3 H	2.64s ^{b}	2.76d ^{b} 2.65d	14 14	2.16s, 3 H	1.58s, 3 H	6.8—8.0m, 14 H			
β	Cl	2.77s ^{b}	2.60s, 3 H	2.82d ^{b} 2.69d	14 14	2.15s, 3 H	2.32s, 3 H	6.8—8.0m, 14 H			
α	Br	2.96s ^{b}	2.71s ^{b}	*b,c*		2.16s, 3 H	1.54s, 3 H	6.8—8.0m, 14 H			
β	Br	2.76s ^{b}	2.68s ^{b}	2.84d ^{b} 2.66d	14 14	2.16s, 3 H	2.47s, 3 H	6.8—8.1m, 14 H			
(2a)	Cl			3.98d 4.16d 2 H	15 15	2.34s,^{d} 3 H		6.5—8.3m, 30 H 9.77dd, 1 H			
(3)	Cl	2.91s ^{b} 2.47s ^{b}	2.75s ^{b} 2.45s ^{b}	*b,c* 3.71d 3.68d 2 H	11 11.4			7.2—7.6m, 8 H	49.0q ^{e}	59.07q	13.8
(7a)	Cl	2.93s, 3 H	2.78s, 3 H	3.08d, 1 H 3.90d, 1 H	12 12			7.2—7.8m, 7 H 8.38dd, 2 H	49.8q	57.8q	15.0
(7b)	Cl	2.88d,^{f} 3 H	2.78d,^{g} 3 H	3.15dd,^{h} 1 H 3.94d, 1H	12 12			7.1—7.6m, 19 H	48.01dq ^{i}	58.66q	13.8
(8a)	Cl			4.27d, 1 H 7.05d, 1 H	14 14			7.3—8.0m, 7 H 8.3dd, 1 H 8.8m, 2 H 9.75dd, 1 H	^{j} 50.63q 53.33q	58.53q 59.95q	14.5 14.0
(8b)	Cl			4.10d, 1 H 6.47d, 1 H	14 14			6.9—8.0m, 19 H 8.35dd, 1 H 9.57m, 1 H	51.26m ^{k}	60.27m ^{k}	13.0
(6)		3.22q,^{l} 3 H						7.0—7.40m, 5 H 6.40d,^{m} 1 H	56.90q	59.50q	15.3

^{a} Chemical shifts (δ) downfield from $SiMe_4$ and upfield from $CFCl_3$ (0.00 p.p.m.) respectively; ^{1}H (90 and/or 250 MHz), ^{19}F [250 MHz and, for (7a) 90 MHz]. s = Singlet; d = doublet; dd = doublet of doublets; q = quadruplet; dq = doublet of quadruplets; m = multiplet. ^{b} Unresolved integration. ^{c} AB quartet overlapped with NMe signals. ^{d} From toluene of crystallization. ^{e} Besides overlapped signals at 49.4q and 49.6m p.p.m.; the bromo-analogue affords only two CF_3 resonances at 48.1m and 58.6q p.p.m., $^5J(F^aF^b)$ 15 Hz, ^{19}F (90 MHz). ^{f} ^4J(P–Me^1) 2.7 Hz. ^{g} ^4J(P–Me^2) 2.0 Hz. ^{h} ^4J(P–H^1) 6.4 Hz. ^{i} ^4J(F^a–P) 8.0 Hz. ^{j} Mixture of stereoisomers, the quartets at 50.63 and at 58.53 p.p.m. correspond to the predominant form (see text). ^{k} Two overlapping quartets. ^4J(F^a–P) 6.5 and ^4J(F^b–P) 19.6 Hz. ^{l} ^5J(F–H) 2.2 Hz. ^{m} ^3J(H–H) 7.8 Hz.

Di-μ-chloro-bis(*NN*-dimethyl-1-naphthylamine-C^8N)-dipalladium reacted with an excess of hfb at room temperature in dichloromethane with a change in colour from yellow to deep orange, but decomposition occurred even under an inert atmosphere. However, red crystals of an organic product were isolated from pentane extracts. The identification of the latter as (6) followed from its molecular weight and spectroscopic data. The mass spectrum contained a parent ion at *m*/*e* 317 together with other ions at *m*/*e* 302 $[P - Me]^+$ and 288 $[P - NMe]^+$. The i.r. spectrum showed typical strong ν(C–F) vibrations between 1 080 and 1 300 cm^{-1} and bands at 1 630s, 1 591ms, and 1 576s cm^{-1} due to ν(C=C). The ^{1}H n.m.r. spectrum revealed, in addition to aromatic proton resonances, a broadened quartet at δ 3.22 p.p.m. (3 H), assigned to the *N*-methyl group. The ^{19}F n.m.r. spectrum consisted of two equally intense 1 : 3 : 3 : 1 quartets centred at 56.90 and 59.60 p.p.m.; the quartets are slightly broadened due to a further small coupling with the *N*-methyl protons. Chemical shifts and coupling constants (Table 2) are consistent with the presence of a *cis*-$CF_3C{=}CCF_3$ group.[23] All attempts to isolate what we believe to be a metallacyclic precursor failed, and the structure depicted for (6) is favoured. It is interesting to note the loss of one of the *N*-methyl groups for the ligand bearing nitrogen as donor atom. This feature has been observed in the reaction of the

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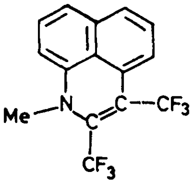
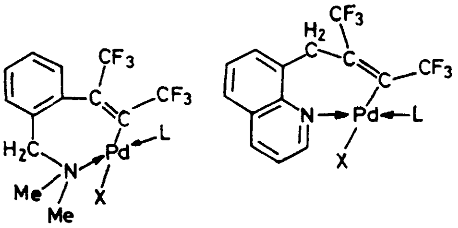
* We thank one of the referees for this suggestion.

NN-dimethylbenzylamine palladated dimer on carbonylation [8] which affords a demethylated product, *i.e.* 2-methylnaphthylamine.



(6)

Bridge-splitting Reactions with Group 5 *Donor-atom Ligands.*—This type of reaction is well known with halide-bridged cyclometallated complexes; [18,22,23,25] thus we have restricted our investigation to some cleavage reactions with neutral unidentate ligands such as triphenylphosphine and pyridine (py). The seven-membered metallacyclic dimers (3) and (4) easily undergo bridge-splitting reactions in CH_2Cl_2 with py and PPh_3 to produce high yields of the monomeric species (7) and (8) respectively. These are more soluble than the corresponding dimeric compounds and accordingly the derivatives of (4), which is insoluble, were more amenable to spectroscopic study.



(7a) L = Py (8a)
(7b) L = PPh3 (8b)

The i.r. spectrum of the monomeric derivatives showed, besides typical absorptions of co-ordinated py or PPh_3, strong absorptions due to ν(C–F) vibrations, bands due to ν(C=C), and one strong band assigned to terminal ν(Pd–X). The range of ν(Pd–X) frequencies, at *ca.* 305—310 and 182—202 cm^{-1} for X = Cl and Br respectively, is consistent with X *trans* to the carbon σ bonded to the metal. These values are somewhat shifted to higher wavenumbers compared to those observed for pyridine or phosphine monomeric derivatives [22,25] of compounds containing only five-membered rings where X is *trans* to alkyl or phenyl groups and for which ν(Pd–X) frequencies occur at 280—299 (X = Cl) and 160—172 cm^{-1} (X = Br). This behaviour can be rationalized in terms of a smaller *trans* influence exerted by an alkenylic carbon than by alkyl or phenyl carbons.[13] The ^1H n.m.r. spectrum of complexes (7a) or (7b) showed, in addition to aromatic proton resonances, two signals of equal intensity assigned to non-equivalent *N*-methyl groups, and the signals from (7b) were consistently split into doublets due to a small coupling of the *N*-methyl protons with phosphorus; the protons associated with the methylene group of most derivatives gave rise to the four lines of an AX system, with the exception of those of (7b) for which one proton is further coupled with phosphorus. The ^{19}F n.m.r. spectrum of each derivative revealed unambiguously that the splitting reactions had occurred with retention of the *cis*-$CF_3C=CCF_3$ group. The spectrum of (8a; X = Cl) showed more clearly than the far-i.r. spectrum that this pyridine complex occurs as a mixture of two stereoisomers, *i.e.* the py is either *cis* or *trans* to the nitrogen atom of the metallacyclic ring (ratio of isomers 8.5 : 1.5). Nevertheless, both the far-i.r. and ^{19}F n.m.r. data indicate that the *trans* derivative (X *trans* to Pd–C σ bond) predominates. The relatively simple ^{19}F n.m.r. spectra of the phosphine derivatives (7b) and (8b) indicated that only one isomeric form occurred in these products, namely the *trans* isomers. Phosphorus–fluorine coupling was observed for both CF_3 groups of (8b), but only for the most proximal CF_3 in (7b). Chemical shifts and important coupling constants are listed in Table 2.

EXPERIMENTAL

Microanalysis was carried out by the C.N.R.S. Microanalytical Service. The i.r. spectra (400—4 000 cm^{-1}) in KBr pellets were recorded on a Beckman IR 12 spectrometer. Spectra in the range 50—420 cm^{-1} were run in polyethylene discs, using a Polytec FIR 30 interferometer. N.m.r. spectra were obtained on Brucker W.H. 90 (90 MHz) and/or Cameca (250 MHz) spectrometers using dichlorodeuteriomethane as the solvent.

Cyclopalladated compounds formed from *NN*-dimethylbenzylamine,[11] 8-methylquinoline,[12] benzo[*h*]quinoline,[12] azobenzene,[19] and *NN*-dimethyl-1-naphthylamine [11] were prepared by published methods. Diphenylacetylene, 1-phenylprop-1-yne, hexafluorobut-2-yne, pyridine, and triphenylphosphine were used as obtained.

Reactions of [{Pd(dmba)X}$_2$] *and* [Pd(dmba)(py)X].—(*a*) *With diphenylacetylene.* A mixture of [{Pd(dmba)X}$_2$] (X = Cl; 0.22 g, 0.4 mmol) and diphenylacetylene (0.30 g, 1.7 mmol) in dichloromethane (60 cm^3) was heated under reflux for 24 h, with rapid stirring. The orange reaction mixture was filtered and then evaporated to dryness *in vacuo*. The resulting solid was exhaustively extracted (Soxhlet) with pentane (200 cm^3) affording a yellow solution which on evaporation at room temperature (r.t.) yielded yellow crystals of (1a; X = Cl). For X = Br the reaction time was shorter (7—8 h) and the crude product was recrystallized from dichloromethane–pentane mixtures to yield light orange crystals of (1a; X = Br). The yield based on Pd was 90% in each case.

(*b*) *With* 1-*phenylprop*-1-*yne.* The compound [{Pd(dmba)X}$_2$] (X = Cl, 0.46 g, 0.83 mmol) and 1-phenylprop-1-yne (0.4 g, 3.4 mmol) were heated under reflux in dichloromethane (60 cm^3) for 20—24 h after which time the solution turned dark orange. After all the solvent had been removed, the crude product was transferred to a frit and quickly extracted with several portions of pentane (*ca.* 20 cm^3) until the last filtrate was colourless or very pale yellow. The combined filtrates afford on standing at r.t. the isomeric α form ($1b_α$) as small lemon-yellow crystals (yield 35—40%). Extraction of the remaining residue in the frit with acetone–pentane (1 : 1) yielded, upon concentration of the solution, a dark yellow product. Further purification was achieved by recrystallization from pure acetone and cooling to −20 °C, affording golden-yellow crystals of the isomeric β form ($1b_{\beta}$) (X = Cl, yield 15—20%), which were collected, washed with excess of pentane, and dried *in vacuo*.

For the bromo-analogues, the crude product was washed twice with pentane (*ca.* 20 cm³), then extracted and repeatedly recrystallized from dichloromethane–pentane (15 : 85) to yield yellow crystals of ($1b_{\beta}$; X = Br), which were collected, washed with portions of cold pentane (*ca.* 5 cm³), and dried *in vacuo*. The combined filtrates were evaporated to dryness *in vacuo*, affording a product which upon repeated recrystallization from acetone–diethyl ether and then from pure acetone yielded dark yellow crystals of the α isomer.

Separation of the two isomers was followed by i.r. analysis. For the bromo-isomers for instance the i.r. peaks in the range 700—800 cm⁻¹ are as follows: ($1b_{\alpha}$) 785m, 769vs, 745w, 738w, 707vs; ($1b_{\beta}$) 774(sh), 767s, 752vs, 741s, and 699vs cm⁻¹.

With the monomeric complexes [Pd(dmba)(py)X] as starting material the procedure was essentially the same except that an excess (20% over the stoicheiometric amount) of acetylene was used.

Reactions of [$\{Pd(8Me\text{-}quin)X\}_2$].—(*a*) *With diphenylacetylene*. A suspension of [$\{Pd(8Me\text{-}quin)Cl\}_2$] (0.46 g, 0.8 mmol) and diphenylacetylene (0.61 g, 3.4 mmol) was heated under reflux in dichloromethane (60 cm³) for 4 d. After evaporation to half-volume the dark orange-red reaction mixture was filtered to remove the insoluble starting material. The resulting filtrate was evaporated to low volume affording yellow crystals which on recrystallization from toluene and cooling to −20 °C yielded (2a; X = Cl) (14%). The combined filtrates were evaporated to dryness to leave a brown solid. This was dissolved in a small volume of dichloromethane and addition of excess of pentane afforded a yellowish precipitate which on recrystallization from acetone yielded colourless crystals of hexaphenylbenzene (25%) identified by its elemental analysis and mass spectrum (molecular ion at *m/e* 534). Repetition of the above experiment using a shorter reaction time gave the bis-insertion product (2a) in variable yield (2 d, 10%; 3 d, 23%).

TABLE 3

Atomic positional parameters (fractional co-ordinates) (× 10⁴) with estimated standard deviations in parentheses for compound ($1b_{\alpha}$; X = Br)

Atom	*x*	*y*	*z*
Pd	3 102.9(0.9)	9 504.3(1.0)	713.8(0.8)
Br	3 506.3(1.7)	7 992.0(1.6)	−228.4(1.4)
C(1)	3 743(11)	10 192(12)	−1 609(11)
C(2)	3 877(13)	10 138(14)	−2 513(12)
C(3)	3 199(13)	10 324(14)	−3 150(11)
C(4)	2 398(14)	10 550(18)	−2 865(11)
C(5)	2 243(12)	10 616(16)	−1 958(11)
C(6)	2 941(11)	10 419(13)	−1 322(10)
C(7)	2 807(10)	10 501(14)	−325(10)
C(8)	2 376(11)	11 283(14)	88(10)
C(9)	1 878(15)	12 296(15)	−240(12)
C(10)	2 497(10)	11 032(12)	1 088(10)
C(11)	1 630(11)	10 887(14)	1 525(11)
C(12)	985(12)	10 177(16)	1 144(13)
C(13)	184(15)	10 033(22)	1 544(18)
C(14)	57(15)	10 594(21)	2 351(16)
C(15)	685(12)	11 333(18)	2 724(13)
C(16)	1 478(12)	11 496(16)	2 311(12)
C(17)	3 315(10)	11 061(12)	1 544(10)
C(18)	4 083(11)	11 572(14)	1 108(11)
C(19)	3 487(10)	10 938(12)	2 545(10)
C(20)	3 313(11)	10 008(13)	3 055(10)
C(21)	3 644(13)	9 993(14)	3 963(13)
C(22)	4 054(12)	10 867(15)	4 404(11)
C(23)	4 159(11)	11 797(14)	3 920(11)
C(24)	3 872(10)	11 820(13)	2 993(10)
C(25)	2 759(11)	9 051(13)	2 717(10)
C(26)	4 061(12)	8 021(15)	2 195(13)
C(27)	2 514(13)	7 507(15)	1 770(14)
N	3 143(9)	8 450(11)	1 945(9)

TABLE 4

Atomic positional parameters (fractional co-ordinates) (× 10⁴) with estimated standard deviations in parentheses for compound ($1b_{\beta}$; X = Cl)

Atom	*x*	*y*	*z*
Pd	2 525.9(1.5)	0	836.5(1.3)
Cl	3 241(6)	−114(7)	3 471(4)
C(1)	3 968(15)	−2 612(24)	−1 506(10)
C(2)	4 265(17)	−3 213(14)	−2 523(9)
C(3)	3 991(16)	−3 069(13)	−4 092(10)
C(4)	3 485(16)	−2 351(21)	−4 620(10)
C(5)	3 209(16)	−1 673(16)	−3 265(15)
C(6)	3 451(14)	−1 810(10)	−2 062(8)
C(7)	3 819(16)	−947(10)	438(15)
C(8)	3 195(16)	−1 102(10)	−1 091(15)
C(9)	5 170(18)	−1 410(11)	1 501(15)
C(10)	2 154(16)	−333(9)	−1 559(13)
C(11)	352(13)	−485(9)	−2 347(13)
C(12)	−662(17)	−1 012(10)	−1 667(16)
C(13)	−2 324(17)	−1 164(10)	−2 356(19)
C(14)	−2 918(17)	−789(10)	−3 732(16)
C(15)	−1 873(16)	−373(8)	−4 433(14)
C(16)	−211(15)	−82(17)	−3 709(13)
C(17)	2 823(17)	422(10)	−1 493(15)
C(18)	4 739(15)	536(11)	−1 378(16)
C(19)	1 859(16)	1 244(9)	−2 063(14)
C(20)	554(17)	1 587(9)	−1 517(14)
C(21)	−92(22)	2 369(15)	−2 056(19)
C(22)	561(22)	2 781(10)	−3 140(20)
C(23)	1 839(21)	2 413(11)	−3 745(17)
C(24)	2 530(16)	1 670(9)	−3 229(15)
C(25)	−433(15)	1 154(10)	−428(14)
C(26)	1 254(20)	1 718(10)	1 905(16)
C(27)	−601(20)	494(13)	2 000(18)
N	598(13)	928(8)	1 126(12)

The bromo-analogue (2a; X = Br) was obtained by metathesis of the chloro-product with an excess of lithium bromide in acetone.

(*b*) *With* 1-*phenylprop*-1-*yne*. The procedure was essentially the same. However, after removal of the insoluble cyclopalladated complex, the filtrate was evaporated to dryness. Extraction with several portions of pure acetone afforded a yellow filtrate and a whitish residue. The latter was dissolved in hot acetone and on cooling yielded a mixture of isomers of trimethyltriphenylbenzene identified by its elemental analysis and its mass (molecular ion at *m/e* 348), and particularly ¹H n.m.r. spectra [methyl resonances observed as two equally intense signals at δ 2.00 (s), 1.675 (s), and 1.66 (s) p.p.m. (Δδ 1.5 Hz)].

An attempt to isolate a pure bis-insertion product from the yellow filtrate in acetone failed. On evaporation to dryness and recrystallization from toluene of the resulting product, the yellow crystals obtained gave rather unsatisfactory analyses (Found: C, 63.9; H, 5.25; N, 2.75. $C_{28}H_{24}ClNPd$ requires C, 65.2; H, 4.5; N, 2.70%). The yield was very poor (0.5—1%).

Reactions of Hexafluorobut-2-*yne*.—(a) *With the* NN-

dimethylbenzylaminepalladium dimer. The complex [{Pd(dmba)X}$_2$] (X = Cl or Br, *ca.* 0.5—0.6 mmol) dissolved in dichloromethane (50 cm^3) was sealed in a thick glass tube with hexafluorobut-2-yne (*ca.* 1.6—2.0 g, 10—12 mmol, condensed at −196 °C) and heated to 60 °C (12—15 h) with a change in colour from yellow to clear orange. The filtered solution afforded, on evaporation at r.t., a deep yellow product which on recrystallization from dichloromethane–pentane mixtures (1 : 1) yielded yellow crystals of (3) (80—90% based on Pd). These were collected, washed with light petroleum, and dried *in vacuo*.

(*b*) *With the* 8-*methylquinolinepalladium dimer*. Similarly a suspension of [{Pd(8Me-quin)Cl}$_2$] (0.26 g, 0.46 mmol) and hexafluorobut-2-yne (1.6 g, 10 mmol) in toluene (60 cm^3) was heated to 60—65 °C (7d) after which time the supernatant solution turned orange. The pale yellow filtered solid (similar to the starting material) was heated with excess of lithium chloride in acetone (25 cm^3). The resulting solution was concentrated to low volume and upon addition of water yielded the pale yellow product (4; X = Cl) which was washed with small portions of ethanol and then with light petroleum and dried (yield 80%). The bromo-analogue (4; X = Br) was obtained by metathesis of (4; X = Cl) with excess of LiBr in acetone.

TABLE 5

Bond lengths (Å) and angles (°) for compound (1b$_\alpha$; X = Br)

(*a*) Distances

Pd–Br	2.449(2)	C(11)–C(12)	1.407(24)
Pd–C(7)	1.999(15)	C(12)–C(13)	1.423(31)
Pd–C(10)	2.199(15)	C(13)–C(14)	1.415(36)
Pd–C(17)	2.295(14)	C(14)–C(15)	1.407(31)
Pd–N	2.247(12)	C(15)–C(16)	1.425(27)
Pd · · · C(8)	2.603(16)	C(16)–C(11)	1.427(24)
Pd · · · A	2.127		
		C(17)–C(18)	1.530(23)
C(1)–C(2)	1.379(25)	C(17)–C(19)	1.499(20)
C(2)–C(3)	1.368(25)		
C(3)–C(4)	1.364(29)	C(19)–C(20)	1.416(22)
C(4)–C(5)	1.393(24)	C(20)–C(21)	1.403(23)
C(5)–C(6)	1.390(22)	C(21)–C(22)	1.388(25)
C(6)–C(1)	1.367(23)	C(22)–C(23)	1.375(24)
		C(23)–C(24)	1.412(21)
C(6)–C(7)	1.519(21)	C(24)–C(19)	1.385(21)
C(7)–C(8)	1.350(23)		
C(8)–C(9)	1.526(25)	C(25)–C(20)	1.519(22)
C(8)–C(10)	1.517(21)	N–C(25)	1.528(20)
C(10)–C(11)	1.541(23)	N–C(26)	1.522(22)
C(10)–C(17)	1.377(20)	N–C(27)	1.523(23)

(*b*) Angles

Br–Pd–C(7)	94.6(0.4)	C(11)–C(12)–C(13)	121.0(1.7)
Br–Pd–N	91.9(0.3)	C(12)–C(13)–C(14)	118.7(1.4)
Br–Pd · · · A	166.8	C(13)–C(14)–C(15)	120.9(1.9)
C(7)–Pd–N	167.9(0.6)	C(14)–C(15)–C(16)	120.3(1.4)
C(7)–Pd · · · A	75.3	C(15)–C(16)–C(11)	119.0(1.1)
N–Pd · · · A	99.6	C(16)–C(11)–C(12)	120.0(1.2)
C(7)–Pd–C(10)	66.0(0.6)		
C(10)–Pd–C(17)	3.56(0.5)	C(10)–C(17)–C(18)	120.4(1.1)
		C(10)–C(17)–C(19)	124.3(1.1)
C(1)–C(6)–C(7)	121.3(1.4)	C(18)–C(17)–C(19)	112.7(0.9)
C(5)–C(6)–C(7)	119.6(1.0)		
		C(17)–C(19)–C(20)	126.1(0.9)
C(2)–C(1)–C(6)	121.9(1.6)	C(17)–C(19)–C(24)	115.6(1.4)
C(1)–C(2)–C(3)	120.0(1.1)	C(19)–C(20)–C(25)	125.6(0.9)
C(2)–C(3)–C(4)	118.2(1.4)	C(21)–C(20)–C(25)	117.1(1.5)
C(3)–C(4)–C(5)	123.0(1.9)		
C(4)–C(5)–C(6)	117.7(1.5)	C(19)–C(20)–C(21)	117.3(1.5)
C(5)–C(6)–C(1)	119.0(1.0)	C(20)–C(21)–C(22)	123.9(1.5)
		C(21)–C(22)–C(23)	118.2(1.3)
C(6)–C(7)–Pd	132.4(0.5)	C(22)–C(23)–C(24)	119.3(1.0)
C(6)–C(7)–C(8)	127.3(1.3)	C(23)–C(24)–C(19)	122.6(1.6)
C(8)–C(7)–Pd	100.2(0.6)	C(24)–C(19)–C(20)	118.3(1.1)
C(7)–C(8)–C(9)	134.0(1.5)		
C(7)–C(8)–C(10)	106.0(1.0)	C(20)–C(25)–N	112.8(0.8)
C(b)–C(8)–C(10)	119.9(1.0)		
		C(25)–N–C(26)	113.2(0.9)
C(8)–C(10)–C(11)	113.6(0.9)	C(25)–N–C(27)	102.8(1.3)
C(8)–C(10)–C(17)	120.6(1.1)	C(26)–N–C(17)	109.7(1.4)
C(11)–C(10)–C(17)	125.5(0.9)	Pd–N–C(25)	110.2(0.9)
		Pd–N–C(26)	111.3(0.8)
C(10)–C(11)–C(12)	120.5(1.2)	Pd–N–C(27)	109.3(1.0)
C(10)–C(11)–C(16)	119.5(0.9)		

TABLE 6

Bond lengths (Å) and angles (°) for compound (1b$_\beta$; X = Cl)

(*a*) Distances

Pd–Cl	2.337(4)	C(11)–C(12)	1.394(19)
Pd–C(7)	1.922(15)	C(12)–C(13)	1.427(18)
Pd–C(10)	2.176(11)	C(13)–C(14)	1.384(21)
Pd–C(17)	2.237(13)	C(14)–C(15)	1.411(20)
Pd–N	2.222(11)	C(15)–C(16)	1.447(17)
Pd · · · C(8)	2.588(14)	C(16)–C(11)	1.389(19)
Pd · · · A	2.104		
		C(17)–C(18)	1.574(19)
C(1)–C(2)	1.372(32)	C(17)–C(19)	1.581(20)
C(2)–C(3)	1.400(12)		
C(3)–C(4)	1.289(35)	C(19)–C(20)	1.364(20)
C(4)–C(5)	1.446(33)	C(20)–C(21)	1.417(26)
C(5)–C(6)	1.394(15)	C(21)–C(22)	1.353(27)
C(6)–C(1)	1.421(38)	C(22)–C(23)	1.389(26)
		C(23)–C(24)	1.369(22)
C(6)–C(8)	1.466(20)	C(24)–C(19)	1.429(19)
C(7)–C(8)	1.400(18)		
C(7)–C(9)	1.532(19)	C(20)–C(25)	1.530(20)
C(8)–C(10)	1.523(19)	N–C(25)	1.547(15)
C(10)–C(11)	1.554(15)	N–C(26)	1.504(19)
C(10)–C(17)	1.328(20)	N–C(27)	1.522(21)

(*b*) Angles

Cl–Pd–C(7)	93.9(0.4)	C(8)–C(10)–C(11)	116.7(1.2)
Cl–Pd–N	90.2(0.3)	C(8)–C(10)–C(17)	121.1(1.2)
Cl–Pd · · · A	166.2	C(11)–C(10)–C(17)	121.4(1.1)
C(7)–Pd–N	168.3(0.5)	C(10)–C(11)–C(12)	119.5(0.8)
C(7)–Pd · · · A	76.2	C(10)–C(11)–C(16)	118.8(0.9)
C(7)–Pd–C(10)	67.6(0.5)		
C(10)–Pd–C(17)	35.0(0.5)	C(16)–C(11)–C(12)	121.7(1.3)
C(17)–Pd–N	95.3(0.5)	C(11)–C(12)–C(13)	121.1(1.2)
N–Pd · · · A	101.4	C(12)–C(13)–C(14)	119.0(0.9)
		C(13)–C(14)–C(15)	119.7(0.9)
C(1)–C(6)–C(8)	124.1(1.2)	C(14)–C(15)–C(16)	121.7(1.3)
C(5)–C(6)–C(8)	117.3(1.2)	C(15)–C(16)–C(11)	116.7(1.5)
C(6)–C(1)–C(2)	118.8(0.9)	C(10)–C(17)–C(18)	120.8(1.1)
C(1)–C(2)–C(3)	121.9(1.6)	C(10)–C(17)–C(19)	124.4(1.0)
C(2)–C(3)–C(4)	120.2(1.1)	C(18)–C(17)–C(19)	111.7(1.0)
C(3)–C(4)–C(5)	121.5(1.7)		
C(4)–C(5)–C(6)	118.9(0.9)	C(17)–C(19)–C(20)	127.2(1.1)
C(5)–C(6)–C(1)	118.6(1.1)	C(17)–C(19)–C(24)	113.7(0.8)
		C(19)–C(20)–C(25)	124.9(0.9)
C(8)–C(7)–Pd	101.2(0.6)	C(21)–C(20)–C(25)	114.2(1.1)
C(9)–C(7)–Pd	129.6(1.0)		
C(8)–C(7)–C(9)	129.2(1.4)	C(24)–C(19)–C(20)	119.0(0.8)
C(6)–C(8)–C(7)	130.5(1.0)	C(19)–C(20)–C(21)	120.7(1.2)
C(6)–C(8)–C(10)	126.6(0.8)	C(20)–C(21)–C(22)	120.4(1.2)
C(7)–C(8)–C(10)	103.0(1.3)	C(21)–C(22)–C(23)	118.9(1.1)
		C(22)–C(23)–C(24)	122.6(1.7)
Pd–N–C(25)	110.6(0.8)	C(23)–C(24)–C(19)	118.3(1.1)
Pd–N–C(26)	114.2(0.6)		
Pd–N–C(27)	106.6(0.5)		
C(20)–C(25)–N	114.0(0.8)		
C(25)–N–C(26)	108.7(1.0)		
C(25)–N–C(27)	105.1(1.1)		
C(26)–N–C(27)	111.3(1.1)		

(*c*) *With the benzo*[h]*quinolinepalladium dimer*. The procedure was essentially the same as for (*b*) except that the solvent was dichloromethane and the reaction time shorter (2 d). The tan product (5; X = Cl) was obtained in rather poor yield (17%). A deep orange filtrate resulting from separation of the reaction mixtures yielded orange crystals which were not identified.

TABLE 7

Some least-squares planes * for compound ($1b_\alpha$; X = Br) and distances (Å) of atoms from planes in square brackets

Plane (*i*): Pd, Br, C(7), N and A, the middle of the C(10)–C(17) vector

$$-0.9540X - 0.2508Y - 0.1643Z + 7.5883 = 0$$

[Pd 0.00010, Br −0.0049, C(7) 0.2533, N 0.1170, A −0.02552]

Plane (*ii*): Pd, C(17), C(19), C(20), C(25), N

$$-0.9777X + 0.2012Y - 0.0591Z - 2.2694 = 0$$

[Pd 0.0005, C(17) 0.0996, C(19) −0.1544, C(20) −0.1057, C(25) 0.4756, N −0.2791]

Plane (*iii*): Pd, C(7), C(8), C(10)

$$-0.8877X - 0.4415Y - 0.1309Z + 9.4855 = 0$$

[Pd 0.0002, C(7) −0.0558, C(8) 0.0711, C(10) −0.0384]

* *X*, *Y*, and *Z* are fractional co-ordinates (Å) in the orthogonal system *a*, *c** × *a*, *c**.

(*d*) *With the* NN-*dimethyl*-1-*naphthylaminepalladium dimer*. A solution of the chloride dimer (0.63 g, 1 mmol) in dichloromethane (50 cm³) was degassed in a glass tube; hexafluorobut-2-yne (1.0 g, 6.2 mmol) was then condensed (−196 °C) into the tube which was sealed *in vacuo*. Reaction takes place at r.t. (10—12 h) with a change in colour from yellow to dark orange but decomposition occurred (formation of Pd^0). The orange-red filtered solution was evaporated to dryness *in vacuo*. Pentane extraction of the crude mixture, under an oxygen-free atmosphere, afforded a deep yellow solution from which red crystals of (6) were isolated by crystallization at −20 °C (variable yield).

TABLE 8

Some least-square planes * for compound ($1b_\beta$; X = Cl) and distances (Å) of atoms from planes in square brackets

Plane (*i*): Pd, Cl, C(7), N, A

$$-0.7123X - 0.7014Y - 0.0268Z + 1.4323 = 0$$

[Pd 0.018, Cl −0.063, C(7) 0.297, N 0.126, A −0.197]

Plane (*ii*): Pd, C(17), C(19), C(20), C(25), N

$$0.5517X - 0.7049Y - 0.4458Z + 1.4358 = 0$$

[Pd 0.028, C(17) 0.144, C(19) −0.170, C(20) −0.137, C(25), 0.460, N −0.238]

Plane (*iii*): Pd, C(7), C(8), C(10)

$$0.8066X + 0.5687Y - 0.1614Z - 1.4800 = 0$$

[Pd −0.020, C(7) 0.075, C(8) −0.085, C(10) 0.048]

* *X*, *Y*, and *Z* are fractional co-ordinates (Å) in the orthogonal system *a*, *c** × *a*, *c**.

Reactions between (3) *or* (4) *and Neutral Ligands* (L = py, *or* PPh_3).—The products of bridge-splitting, (7) and (8), were obtained in high yield (*ca.* 75—85%) from the following general procedure. The dimer (3) or (4) (*ca.* 1 mmol) was treated with a 15—20% excess (>2 mmol) of L (py or PPh_3) in dichloromethane (30 cm³) with stirring at r.t. until the solid dissolved (*ca.* 2—3 min). The clear solution was evaporated to low volume at r.t. and addition of light petroleum yielded a fine precipitate of the product. Purification was accomplished by recrystallization from dichloromethane–light petroleum.

Crystal-structure Determination of [Pd(CMe=CPhCPh=CMe$C_6H_4CH_2NMe_2$)Cl] ($1b_\beta$; X = Cl) *and of* [Pd(CPh=CMeCPh=CMe$C_6H_4CH_2NMe_2$)Br] ($1b_\alpha$; X = Br).—Crystallographic data were recorded at room temperature (20 °C) on a Nonius CAD-4 automatic diffractometer, using graphite-monochromated Mo-K_α radiation (λ 0.710 69 Å). We chose sufficiently small crystals so that the *X*-ray absorption corrections could be neglected. The unit-cell parameters were obtained from the setting angles of 15 reflections, and intensity data were collected in the range $2 < \theta < 30°$, using an ω—2θ scan of width $S = (1.20 + 0.30\tan\theta)°$ and a counter aperture $D = (3.00 + 0.1\tan\theta)$ mm.[16] Data reduction was performed with the program MAXE.[26]

Crystal data. $C_{27}H_{28}BrNPd$, $M = 552.8$, Monoclinic, $a = 15.362(13)$, $b = 12.368(5)$, $c = 14.886(11)$ Å, $\beta = 94.86(13)°$, $U = 2\,818$ Å³, $Z = 4$, $D_c = 130$ g cm⁻³, μ(Mo-K_α) = 21.6 cm⁻¹, $F(000) = 1\,112$, space group $P2_1/c$ (no. 14), 2 529 independent reflections, where $\sigma(I)/I < 1/3$, retained for the the structure refinement.

$C_{27}H_{28}ClNPd$, $M = 508.4$, Monoclinic, $a = 8.227(6)$, $b = 16.059(33)$, $c = 8.923(9)$ Å, $\beta = 99.30(12)°$, $U = 1\,163.4$ Å³, $Z = 2$, $D_c = 1.45$ g cm⁻³, μ(Mo-K_α) = 9.7 cm⁻¹, $F(000) = 520$, space group $P2_1$ (no. 4), 2 077 independent reflections with $\sigma(I)/I < 1$ retained for the structure refinement.

Structure solution and refinement. The molecular structures were solved from Fourier-difference synthesis, following location of the heavy atoms (Pd and X = Cl or Br) and several carbon atoms with the program MULTAN.[27]

The refinement of the atomic co-ordinates together with the thermal parameters, isotropic at first then anisotropic, of the 30 atoms (excluding hydrogen) of the molecule gave the final values of R $[= \Sigma(|F_o| - K|F_c|)/\Sigma|F_o|]$ of 0.074 and 0.078 and of R' $\{= [\Sigma w(|F_o| - K|F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ of 0.065 and 0.105 for ($1b_\beta$; X = Cl) and ($1b_\alpha$; X = Br) respectively. We used a weighting scheme of the Ibers type. With the exception of those of the methyl groups, all the hydrogen atoms were located on difference-Fourier synthesis and included in their calculated positions, but not refined in the latter stages of refinement. They were assigned isotropic thermal parameters equivalent to those of the carbon atoms to which they were bonded. The least-squares refinements were performed using SFLS-5.[28]

Atomic positional parameters are in Tables 3 and 4, interatomic distances and angles in Tables 5 and 6, and selected least-squares planes in Tables 7 and 8. Observed and calculated structure factors, all the thermal parameters, the shortest intermolecular distances, and details of the phenyl-ring planes are listed in Supplementary Publication No. SUP 22416 (22 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S.Dalton*, 1978, Index issue.

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