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PALLADIUM ASSISTED ORGANIC REACTIONS

III *. THE PREPARATION OF DI-μ-CHLOROBIS-(*N*,*N*-DIALKYLBENZYLAMINE-2,C,N)DIPALLADIUM(II) COMPLEXES

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Summary

The preparation and ^{1}H NMR spectra of some di-μ-chloro-bis(*N*,*N*-dialkylbenzylamine-2,C,N)dipalladium(II) complexes, and the corresponding monomeric triphenylphosphine derivatives are described. A reaction sequence is presented for the cyclopalladation reaction and some improved conditions for the preparation of these complexes are presented.

Introduction

The first di-μ-chloro-bis(*N*,*N*-dialkylbenzylamine-2,C,N)dipalladium(II) complex (I) was prepared by Cope and Friedrich [2] who treated *N*,*N*-dimethylbenzylamine with Li_2PdCl_4 in methanol solution at room temperature for several hours. Since then a number of similar complexes has been prepared [1,3–6] by essentially the same method. Complexes of type II are not formed under these conditions, although they have been prepared by others methods [7]. The sequence III → IV → V has also been described [8], although the final ring-closure to VI could not be achieved.

It has been shown by IR [9] and X-ray studies [10] that these chloride-bridged dimers have the *trans* geometry depicted in I. This is also the case in most of the corresponding acetate-bridged dimers, where only one C-methyl resonance appears in the ^{1}H NMR spectrum. Cyclopalladation of tertiary benzylamines has been shown to be regiospecific [1,5,11].

It is generally accepted [2–4] that cyclopalladation involves initial, rapid coordination of the nitrogen lone pair to the palladium atom, followed by an electrophilic substitution by the palladium on to the aromatic ring. The usual considerations

* For part II see ref. 1.

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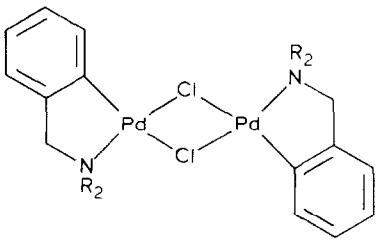
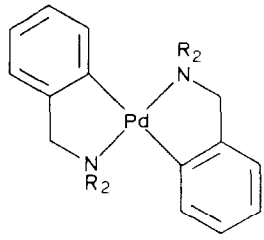


(I)



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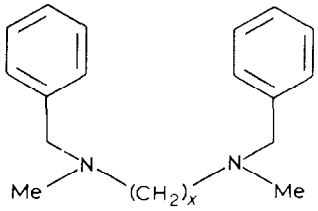
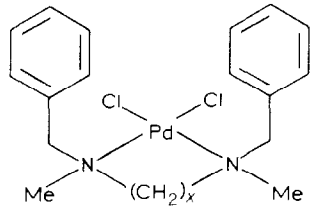


(III)

(x = 2 or 3)



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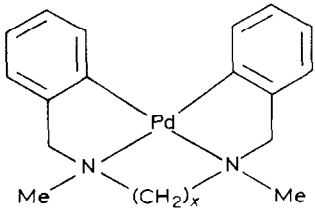

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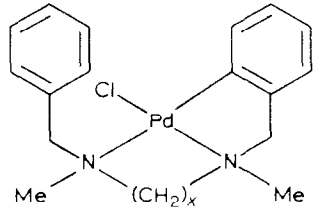


(V)

quoted in support of this concept include: (a) although cyclopalladation occurs readily with *N*,*N*-dimethylbenzylamine itself, no such reaction is observed with the *p*-nitro-compound [2]; (b) the order of reactivities in *p*-substituted azobenzenes (which also undergo cyclopalladation) decrease in the order OMe > H > Cl [4]; (c) in asymmetrically substituted azobenzenes, the electron-rich ring is preferentially palladated [12] and (d) the rate of palladation of *N*,*N*-dialkylbenzylamines is greater than that of azobenzenes [12]. No more detail has been forthcoming.

Experimental

^{1}H NMR spectra were recorded at 60 MHz for solutions in $CDCl_3$. Chemical shifts are expressed relative to internal TMS. Melting points are uncorrected.

Preparation of the bridged chloride dimers

Method 1. The benzylamine (6.8 mmol) in MeOH (25 ml) was treated with 0.34 *M* Li_2PdCl_4 (10 ml) in MeOH. After 24 h at r.t. (24–33°C) the solid was collected, washed with a little MeOH and dried at r.t. The complex was dissolved in hot $CHCl_3$ and filtered through a column of Celite to remove Pd(0) residues, and the filtrate was crystallised from $CHCl_3$ or $CHCl_3$/MeOH.

Method 2. $PdCl_2$ (1.77 g; 0.01 mol) was mixed with LiCl (0.43 g; 0.01 mol) in MeOH (50 ml) at r.t. The mixture was heated to boiling to effect dissolution, then, whilst hot, this solution was added to a solution of the benzylamine (0.02 mol) in MeOH (50 ml). After stirring for 10 min the solid product was collected, washed with a little MeOH, dried in vacuo at r.t. and crystallised as stated above.

Method 3. A solution of the benzylamine (2.0 mmol), and $(PhCN)_2PdCl_2$ (1.0 mmol) in MeOH (50 ml) was stirred at r.t. for 24 h. The solid product was purified as above.

The analytical data for the compounds prepared are summarised in Table 1. Satisfactory data were not obtained for all the complexes but all were characterised as the triphenylphosphine derivative (see Table 1).

Preparation of triphenylphosphine complexes

The bridged chloride dimer (0.5 mmol) was mixed with triphenylphosphine (1.1 mmol) in CH_2Cl_2 (10 ml). After 30 min the solution was filtered through Celite, and the Celite washed with a little CH_2Cl_2. To the combined CH_2Cl_2 solutions hexane was added and the resulting precipitate was collected and crystallised from hot CH_2Cl_2/hexane.

Results and discussion

Assuming that the reagent used for the cyclopalladation ($LiCl/PdCl_2$ ratio 2/1 in methanol) is Li_2PdCl_4, as generally supposed (but see below), there are several possible pathways for the reaction to proceed to the chloride-bridged dimer; the main ones are summarised in Scheme 1. The first-formed intermediate VII may undergo cyclopalladation to give the anion VIII, which could then dimerise to the observed product I. This is the route that has been suggested [13,14] for the cyclopalladation of azobenzene. A second route would involve the dimerisation of VII to give XI which may then undergo successive cyclopalladation reactions to XII and then to I. A third possibility is for the first-formed intermediate VII to react with a second molecule of the benzylamine to yield the *trans*, neutral complex IX. Such complexes are known [2]. Intramolecular cyclopalladation of IX would lead to X, followed by chloride-bridged dimer I formation, and the release of one molecule of the benzylamine. It is also possible for the complex IX to dimerise to XI. All of these pathways require a ratio of amine/Pd of 2/1; Cope and Friedrich [2] did find that best yields of cyclopalladated complexes were obtained with this ratio.

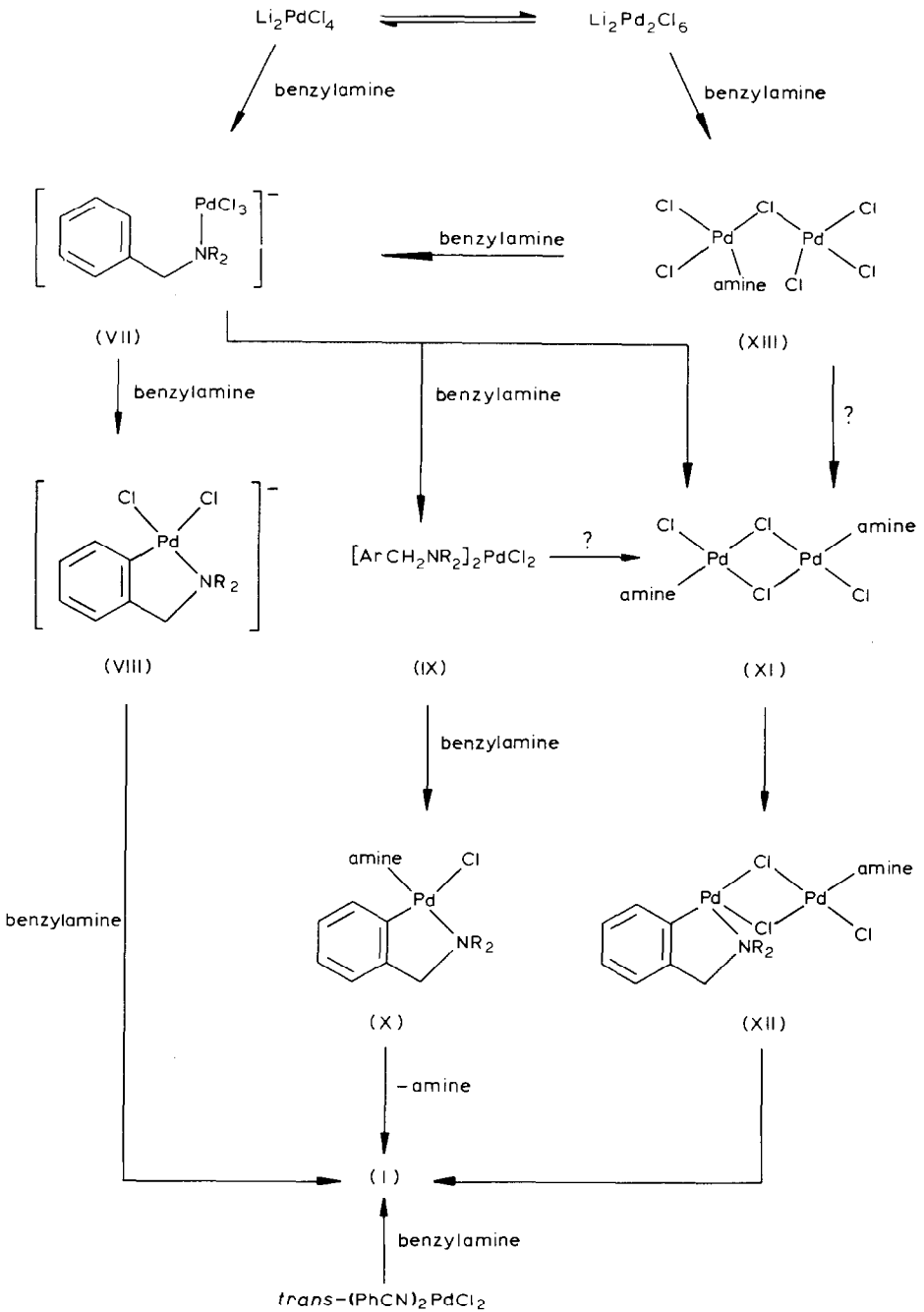
In our experiments we, too, have used a ratio of benzylamine/Pd of 2/1, when

TABLE 1

CHARACTERISATION OF THE COMPLEXES

No. [a]	M.p. (°C)	Yield(%) (Method) [b]	Molecular formula	Analyses (Found(calcd.)(%)) [c]			
				C	H	N	Cl
20	178	88.0 (1)	$C_{20}H_{28}Cl_2N_2O_2Pd_2$	38.6 (39.2)	4.6 (4.6)	4.3 (4.6)	12.5 (11.6)
21	201.5	–	$C_{28}H_{29}ClNOPPd$	59.0 (59.2)	5.2 (5.1)	2.4 (2.5)	6.5 (6.2)
22	156	99.9 (1)	$C_{20}H_{28}Cl_2N_2O_2Pd_2$	39.2 (39.2)	4.6 (4.6)	4.7 (4.6)	– (11.6)
23	180	–	$C_{28}H_{29}ClNOPPd$	58.9 (59.2)	5.2 (5.1)	2.4 (2.5)	6.1 (6.2)
24	173	92.0 (2)	$C_{20}H_{28}Cl_2N_2O_2Pd_2$	38.6 (39.2)	4.55 (4.6)	4.5 (4.6)	12.5 (11.6)
25	203	–	$C_{28}H_{29}ClNOPPd$	58.7 (59.2)	5.15 (5.1)	2.5 (2.5)	6.8 (6.2)
28	180	97.0 (1)	$C_{22}H_{32}Cl_2N_2O_4Pd_2$	39.3 (39.3)	4.9 (4.8)	4.2 (4.2)	10.7 (10.55)
29	199.5	–	$C_{29}H_{31}ClNO_2PPd$	58.1 (58.2)	5.3 (5.2)	2.3 (2.3)	6.1 (5.9)
30	175.5	96.0 (1)	$C_{22}H_{32}Cl_2N_2O_4Pd_2$	38.9 (39.3)	4.8 (4.8)	4.15 (4.2)	10.5 (10.55)
31	84.5	–	$C_{30}H_{33}Cl_3NO_2PPd$ [d]	52.9 (52.7)	4.7 (4.9)	2.0 (2.05)	14.7 (15.6)
32	168	87.0 (1)	$C_{24}H_{36}Cl_2N_2O_6Pd_2$	39.0 (39.4)	4.95 (5.0)	3.8 (3.8)	10.7 (9.7)
33	191	–	$C_{30}H_{33}ClNO_3PPd$	56.85 (57.3)	5.3 (5.3)	2.2 (2.2)	6.4 (5.6)
34	184	92.0 (2)	$C_{20}H_{24}Cl_2N_2O_4Pd_2$	37.5 (37.5)	3.8 (3.8)	4.3 (4.4)	11.2 (11.1)
35	187	–	$C_{28}H_{29}ClNO_2PPd$	57.5 (57.75)	4.7 (4.7)	2.3 (2.4)	6.5 (6.1)
36	157	95.0 (1)	$C_{24}H_{36}Cl_2N_2O_2Pd_2$	43.0 (43.1)	5.45 (5.4)	4.1 (4.2)	11.0 (10.6)
37	182	–	$C_{30}H_{33}ClNOPPd$	60.1 (60.4)	5.5 (5.6)	2.3 (2.35)	6.0 (5.9)
38	143	93 (1)	$C_{28}H_{40}Cl_2N_2O_4Pd_2$	41.5 (41.4)	4.7 (4.6)	4.0 (4.0)	10.1 (10.2)
39	184	–	$C_{32}H_{35}ClNO_2PPd$	59.4 (59.4)	5.7 (5.6)	2.2 (2.2)	5.5 (5.7)
40	160	99.8 (1)	$C_{24}H_{32}Cl_2N_2O_4Pd_2$				
41	192	–	$C_{30}H_{31}ClNO_2PPd$	58.8 (59.0)	5.2 (5.1)	2.2 (2.3)	6.0 (5.8)
42	169	97.6 (1)	$C_{22}H_{28}Cl_2N_2O_4Pd_2$	39.35 (39.55)	4.3 (4.2)	4.2 (4.2)	10.6 (10.6)
43	182	–	$C_{29}H_{31}ClNO_2PPd$	58.2 (58.4)	4.9 (4.9)	2.4 (2.35)	5.95 (5.9)

[a] See Table 2 for identification of the complexes 20–43. [b] See Experimental. [c] In some cases the bridged dimers did not give completely satisfactory analyses. [d] 1 mol of CH_2Cl_2 of crystallisation.



SCHEME 1. The cyclopalladation of *N*,*N*-dialkylbenzylamines.

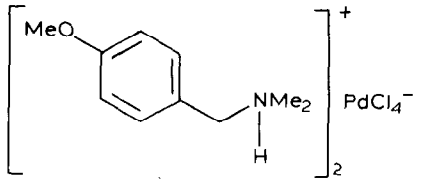
yields of cyclopalladated materials were high in almost all cases (see Table 1). In general our reactions were complete in a much shorter time than that found previously [2] ("room temperature" was 26–30°C), and yields were often higher. For example, with *N*,*N*-dimethyl-3,5-dimethoxybenzylamine Cope and Friedrich [2]

reported 66% yield, whereas we found 97%. The previous workers [2] reported 50% yield of cyclopalladated dimer when *N*,*N*-dimethyl-*p*-methoxybenzylamine was used, together with an unspecified quantity of a benzene-insoluble material formulated as the hydrochloride of the dichlorobis(amine)palladium(II) complex IX, (Ar = *p*-$MeOC_6H_4$; R = Me). A more probable structure for this product is XIV, especially since a ratio of benzylamine/Pd of 1/1 was used in this case. Using our standard conditions (see Experimental) with the same amine we found that a compound precipitated rapidly (5–10 min) in high yield. The ^1H NMR spectrum showed clearly that cyclopalladation had not occurred, and we believe this compound is IX, (Ar = *p*-$MeOC_6H_4$; R = Me). However, when attempts were made to purify it, the chloride-bridged dimer, together with one mol of benzylamine, was obtained. This same change could be followed by UV and ^1H NMR spectral measurements. Since this change occurred in the absence of free benzylamine, it might proceed through the dimers of type XI and XII; the conversion of IX to X requires a mol of benzylamine to be present, assuming HCl must be consumed. We also have isolated XIV, and, when this is reacted with two mol of the benzylamine the bridged dimer and benzylamine hydrochloride are formed. A different type of intermediate was isolated when the glycine ester XV [5] was treated with $LiCl/PdCl_2$ mixture in methanol. The ^1H and ^{13}C NMR [15] spectra are compatible with either structure XVI or XVII for the material that precipitates rapidly from solution, but elemental analyses favour the latter [5]. Dissolution of this material in $CDCl_3$ at 33°C caused production of the chloride-bridged dimer described previously [5], together with a mol of free amine XV. The same dimer was produced when a solution of the amine XV in methanol was treated with *trans*-$(PhCN)_2PdCl_2$. Curiously, we found that *N*,*N*-dimethyl-3,4-methylenedioxybenzylamine gave very poor yields of cyclopalladated material under our standard conditions, whereas the *N*,*N*-diethyl and *N*-methyl-*N*-ethyl analogues behaved normally.

For solutions of LiCl and $PdCl_2$ in acetic acid it has been found [16] that the equilibrium

$$2LiCl + Li_2Pd_2Cl_6 \rightleftarrows 2Li_2PdCl_4 \qquad (1)$$

is important, with the species $Li_2Pd_2Cl_6$ predominating at low concentrations of LiCl. The hexachloropalladate anion is almost certain to be the chloride-bridged species XVIII. There is evidence [17–19] that such a dimer exists in other solvents of low dielectric constant, but not in water. We have some evidence to support the existence of this dimer in methanol solution. A second important equilibrium for acetic acid solution is $2LiCl \rightleftarrows Li_2Cl_2$, for which $K_D = 2.4\ M^{-1}$ at 37.5°C. A similar equilibrium seems reasonable for methanol solutions, so, even with a ratio of $LiCl/PdCl_2$ of 2/1, the predominant species in solution should be $Li_2Pd_2Cl_6$. Since the rate of nucleophilic substitution by amines is greater with the hexachloropalladate ion than with the monomeric tetrachloropalladate (to give initially a complex of type XIII, see Scheme 1), the very first step in the reaction may be the production of XIII. It is possible that the dimer XI is formed from this at least in some cases. However, reaction of XI with a second molecule of benzylamine would yield VII, and the cyclopalladation may then proceed as discussed previously. We reasoned that if the concentration of $Li_2Pd_2Cl_6$ could be increased, the rate of reaction would also increase, and this might then lead to a more facile synthesis of the chloride-bridged dimers I. In the event we have found that by using a $LiCl/PdCl_2$ ratio of



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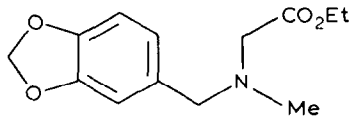

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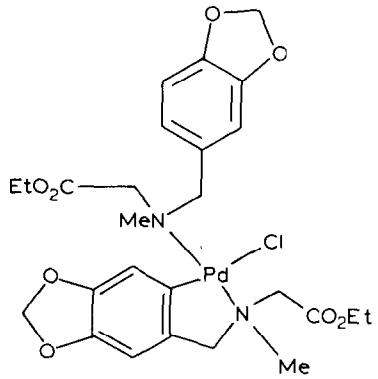

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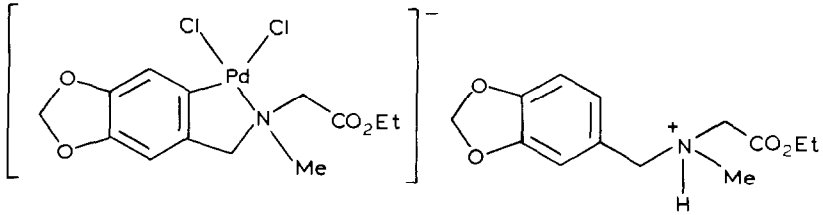
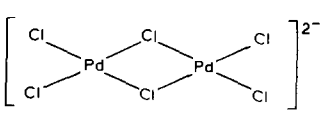


(XVII)

1/1, cyclopalladation occurred more rapidly and in higher yields than under the standard conditions with all amines studied except XV. In particular, with *N*,*N*-dimethyl-3,4-methylenedioxybenzylamine the yield of the complex has been raised from about 1 to > 90%. However, with the amine XV only black tars containing metallic palladium were formed under these new conditions, possibly because of interactions between the palladium atom, which would be held more rigidly in an intermediate such as XI rather than VIII or X, and the ethoxycarbonyl group.



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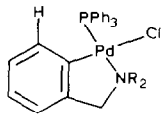


(XIX)

TABLE 2

^{1}H NMR SPECTRAL DATA FOR THE COMPLEXES [a]

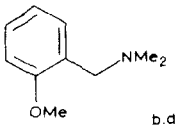
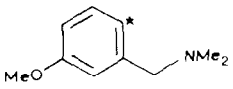
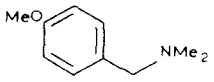
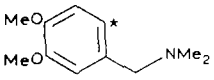
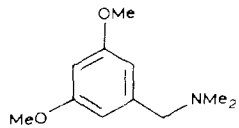
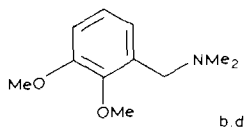
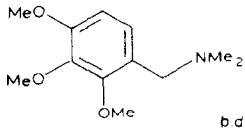
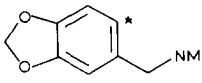
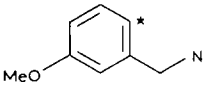
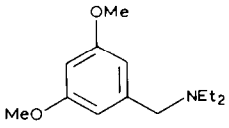
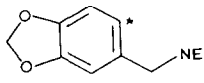
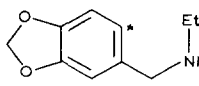
Compound	No.	C_5-H [d]	Other Ar-H [d]	OMe [d] or CH_2O_2	$ArCH_2N$ [d]	N–Me [d] or $N–CH_2R$
		7.37–6.63m		3.75	3.47	2.25
b.d. [b]	20	6.5m		3.73	3.98	2.87
TPP [c]	21	6.0m		3.68	4.1d *J* 2.0 Hz	2.83d *J* 2.5 Hz
		7.30–6.57m		3.70	3.32	2.20
b.d.	22	6.35m		3.70	3.87	2.83
TPP	23	6.1m		3.60	4.03d *J* 2.0 Hz	2.85d *J* 2.6 Hz
★ position of cyclopalladation						
		7.33–6.67m		3.68	3.30	2.18
b.d.	24	6.85–6.38m		3.73	3.87	2.82
TPP	25	5.93m		2.98	4.03bs	2.85bs
		6.85 and 6.75		3.83 3.78	3.32	2.20
	26	6.50	6.70	3.85 3.80	3.90	2.87
b.d. TPP	27	5.92d *J* 6.5 Hz	6.63	3.78 2.92	4.05d *J* 2.0 Hz	2.88
		7.30–6.27m		3.75	3.35	2.22
	28	6.12d *J* 2.0 Hz	6.32d *J* 2.0 Hz	3.73 3.68	3.87	2.82
b.d. TPP	29	5.55bs	5.98d	3.65	4.05bs	2.85d *J* 2.5 Hz
		7.30–6.27m		3.75	3.35	2.22
	30	6.50d *J* 9.0 Hz	6.80d *J* 9.0 Hz	3.45 3.40	4.00	2.83
b.d. TPP	31	5.93m	6.00d	3.75 3.62	4.15d *J* 2.0 Hz	2.83d *J* 2.5 Hz
		6.93d *J* 8.0 Hz	or 6.57d *J* 8.0 Hz	3.90 3.87 3.85	3.35	2.23
b.d.	32	6.52		3.83	4.00	2.87
TPP	33	5.75m		3.83 3.75 2.87	4.13	2.87

TABLE 2 (continued)

Compound	No.	C_5-H [d]	Other Ar-H [d]	OMe [d] or CH_2O_2	$ArCH_2N$ [d]	N-Me [d] or $N-CH_2R$
		6.80 or 6.72		5.87	3.30	2.20
b.d.	34	6.45	6.87	5.83	3.87	2.83
TPP	35	5.82d *J* 6.6 Hz	6.60	5.62	4.00d *J* 2.2 Hz	2.83d *J* 2.7 Hz
		7.37–6.60m		3.77	3.53	2.53q
b.d.	36	7.20–6.33m		3.73	3.93	2.97q
TPP	37	6.67–5.83m		3.63	4.10d *J* 2.0 Hz	3.7–2.5m
		6.60–6.27m		3.77	3.50	2.53q
	38	6.02d *J* 2.5 Hz	6.22d *J* 2.5 Hz	3.73 3.72	4.00	2.78m
b.d. TPP	39	5.53dd	6.32d *J* 2.4 Hz	3.68 2.48	4.12d *J* 2.0 Hz	3.3–3.6m
		6.87 and 6.73		5.90	3.47	2.5q
b.d.	40	6.47	6.73	5.83	3.90	2.85m
TPP	41	5.82d *J* 6.5 Hz	6.60	5.60	4.05d *J* 2.1 Hz	2.5–2.6m
		6.68–6.80		5.82	3.33	2.13s 2.40q
	42	6.47	6.73	5.87	3.90	2.77s 2.88q
b.d. TPP	43	5.81d *J* 6.2 Hz		5.57	4.00dd	2.85d 2.88q

[a] δ values, $CDCl_3$ solution. [b] Bridged chloride dimer. [c] Triphenylphosphine monomer. [d] Singlets unless otherwise stated.

In all cases where a choice existed, cyclopalladation occurred regiospecifically to the 6-position, as deduced from an examination of the ^1H NMR spectra of the chloro-bridged dimer, or, more usefully, from the monomeric triphenylphosphine derivative of type XIX. It was noted in early studies [2] that considerable downfield shifts of hydrogen occurs when it is attached to carbon atoms α to nitrogen. We have confirmed this observation. It can be seen from Table 2 that downfield shifts of about 0.6 ppm (compared with the free amine) have occurred in both the bridged chloride dimers and the derived triphenylphosphine monomeric complexes for the $N-CH_3$ and the $Ar-CH_2-N$ resonances.

In the triphenylphosphine complexes large upfield shifts of some aromatic hydrogen atoms have been noted [10], indicating that this ligand is *trans* to nitrogen. From Table 2 it can be seen that the C_5-H absorbs at δ5.8–5.9 ppm, an upfield shift of 0.8–1.0 ppm. Long-range couplings of protons to ^{31}P have also been observed and confirmed in the present study. In particular the ^{31}P to C_5-H coupling is 6.2–6.6 Hz, whereas the ^{31}P to Ar–CH_2–N and N–CH_3 couplings lie in the range 2.0–2.2 and 2.5–2.7 Hz, respectively. Irradiation of the ^{31}P resonance caused all three hydrogen doublet resonances to collapse to singlets [20].

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