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PALLADIUM ASSISTED ORGANIC REACTIONS

VII*. THE PREPARATION OF CYCLOPALLADATED PRIMARY AND SECONDARY BENZYLAMINES

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Summary

A new method is described for the preparation of cyclopalladated benzylamines, involving the reaction of the *ortho*-bromobenzylamines with bis(dibenzylideneacetone)palladium(0). By using this method cyclopalladated complexes of simple primary and secondary benzylamines have been obtained for the first time. These complexes have been fully characterised as either the monomeric bromo(benzylamine-6-*C*,*N*)triphenylphosphinepalladium(II) derivatives or as the corresponding acetylacetonates. ^1H and ^{13}C NMR spectral data have been obtained and, in most cases, full assignments have been made.

Introduction

The first cyclopalladated benzylamine complexes were described by Cope and Friedrich [2], who established that the nitrogen must be tertiary, and substituents on the benzene ring (if present) must be electron-donating, rather than electron-withdrawing, in nature. They found that, with primary or secondary benzylamines, the complexes formed were of the type $(ArCH_2NHR)_2PdCl_2$. Almost all of the work reported since that time has been concerned with t-benzylamines [3], although it has been reported [4] that the secondary amine *N*-methyl-*N*-triphenylmethylamine, and the primary amine triphenylmethylamine undergo cyclopalladation. This was attributed to steric factors. Because the metal–carbon bond in the chelated tertiary benzylamines undergo an "insertion" reaction with, for example, carbon monoxide [5,6], electron-deficient alkenes [7–9], alkynes [10] and acyl halides [11,12] regiospecifically, they have begun to attract interest in organic synthetic methodology.

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However, since the cyclopalladation reaction has, until now, been restricted to tertiary benzylamines, the products obtained from the insertion reactions have provided little scope for further elaboration into more complex homo or heterocyclic structures [12,13].

We describe, in this paper, a method for the preparation of cyclopalladated primary and secondary benzylamines, which seems to be quite general, and which occurs in good to excellent yields [14].

Experimental

The primary benzylamines were prepared by the reduction of the corresponding oximes with zinc in acetic acid at 60–70°C and the secondary benzylamines by reduction of the corresponding imines [1] with $NaBH_4$. All amines where characterised by GC-MS and by ^1H and ^{13}C NMR spectra using the instrumentation described previously [1].

The di-μ-bromo-bis(benzylamine-6-*C*,*N*)dipalladium(II) complexes (**2**) and the derived monomeric bromo(benzylamine-6-*C*,*N*)triphenylphosphinepalladium(II) compounds (**3**) were prepared under the same conditions as those described for the benzalimine complexes [1]. A typical preparation of an acetylacetonate complex (**4**) is illustrated for acetylacetanato-(3,4-dimethoxybenzylamine-6-*C*,*N*)palladium(II) (**4a**): To a stirred solution of sodium acetylacetonate (from 0.2 g (8.7 g atom) of sodium and 4 ml of acetylacetone in 30 ml of anhydrous methanol) was added di-μ-bromo-bis(3,4-dimethoxybenzylamine-6-*C*,*N*)dipalladium(II) (**3a**) (0.6 g, 0.85 mmol) at room temperature. The solution was stirred overnight, the precipitate was collected and washed with methanol. The resultant off-white solid was dissolved in methylene chloride, filtered through celite, and crystallised by the addition of methanol. The white crystalline product was collected, washed with methanol and dried in air to yield 0.18 g (28%) of product.

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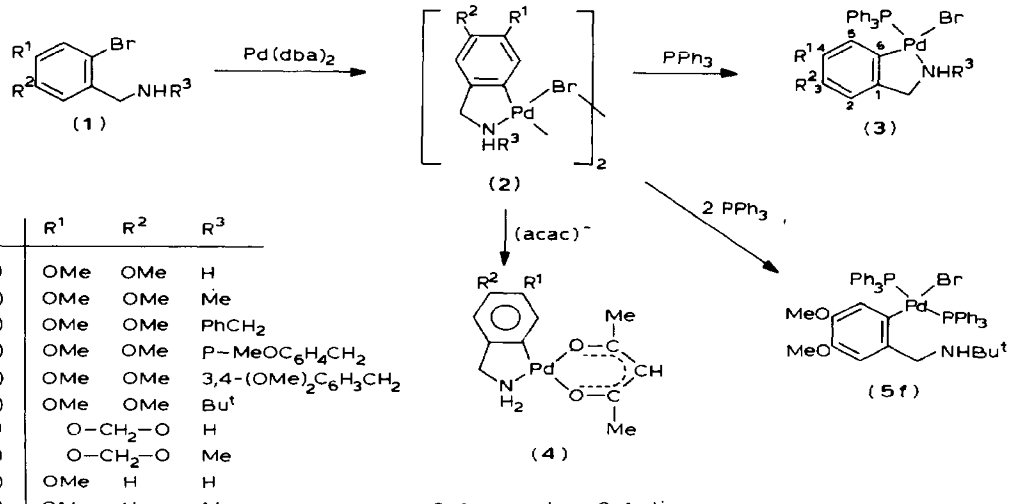
SCHEME 1



	R¹	R²	R³
(a)	OMe	OMe	H
(b)	OMe	OMe	Me
(c)	OMe	OMe	$PhCH_2$
(d)	OMe	OMe	$p-MeOC_6H_4CH_2$
(e)	OMe	OMe	$3,4-(OMe)_2C_6H_3CH_2$
(f)	OMe	OMe	Bu^t
(g)	$O-CH_2-O$		H
(h)	$O-CH_2-O$		Me
(i)	OMe	H	H
(j)	OMe	H	Me
(k)	H	H	H
(l)	H	H	Me

acac = pentan-2,4-dione
dba = dibenzylideneacetone

TABLE 1

ANALYTICAL DATA

Compound	Molecular formula	Found (calcd.) (%)				Mol.wt. Found (calcd.)	ν(NH) Monomer [a] (Parent dimer)	% Yield monomer (Parent dimer)
		C	H	N	X			
2b	$C_{20}H_{28}Br_2N_2O_4Pd$	32.7	3.9	3.7	21.9			(97)
		(32.8)	(3.85)	(3.8)	(21.8)			
3a	$C_{27}H_{27}BrNO_2PPd$	52.4	4.4	2.5	13.2	592	3235, 3325	42
		(52.7)	(4.4)	(2.3)	(13.0)	(615)	(3280)	(89)
3b	$C_{28}H_{29}BrNO_2PPd$	53.6	4.7	2.2	12.6	595	NM	85
		(53.5)	(4.65)	(2.2)	(12.7)	(629)	NM	(97)
3c	$C_{34}H_{33}BrNO_2PPd$	57.9	4.6	2.2	11.4		3268vw	74
		(57.9)	(4.7)	(2.0)	(11.3)		(3200)	(84)
3d	$C_{35}H_{35}BrNO_3PPd$	57.4	4.75	2.0	11.2		3261	80
		(57.2)	(4.8)	(1.9)	(10.9)		(3205vw, 3248vw)	(99)
3e	$C_{36}H_{37}BrNO_4PPd$	57.0	5.0	1.75	10.6		NM	43
		(56.5)	(4.9)	(1.8)	(10.5)		(3195)	(88)
3f	$C_{31}H_{35}BrNO_2PPd$	56.1	5.45	1.9	11.4	660	3245vw	90
		(55.5)	(5.25)	(2.1)	(11.9)	(671)	(3170)	(97)
3g	$C_{26}H_{23}BrNO_2PPd$	52.4	3.85	2.2	13.1		3250	28
		(52.2)	(3.9)	(2.3)	(13.4)		(3122, 3191, 3245, 3295)	(98)
3h	$C_{27}H_{25}BrNO_2PPd$	53.2	4.1	2.2	12.7		3150	85
		(52.9)	(4.1)	(2.3)	(13.0)		(3180, 3225)	(77)
3j	$C_{27}H_{27}BrNOPPd$	54.2	4.7	2.2	12.9		3205	85
		(54.2)	(4.55)	(2.3)	(13.3)		(3190)	(58)
4a	$C_{14}H_{19}NO_4Pd$	45.6	5.2	3.8		366	3205, 3260	29
		(45.2)	(5.15)	(3.8)		(372)		(89)
4i	$C_{13}H_{17}NO_3Pd$	45.5	5.0	4.1			3248, 3295	12
		(45.7)	(5.0)	(4.1)			(absent)	(75)
4k	$C_{12}H_{15}NO_2Pd$	45.9	4.7	4.45			NM	24
		(46.2)	(4.85)	(4.5)			(3120w, 3180w)	(94)

[a] Medium intensity if not stated. w = weak; vw = very weak; NM = not measured.

TABLE 2

^{1}H NMR SPECTRAL DATA (δ in ppm; J in Hz)[a]

Compound	δ(Ar)		δ(C(3)OMe)	δ(C(4)OMe)	δ(ArCH$_2$N)		δ(Me)	δ(NH)	Other
	2	5							
3a	6.60	5.92(d) $J(\mathrm{PH})$ 6.35	3.75	2.83	H(s) 4.31 $J(\mathrm{PH})$ 2.78 $J(\mathrm{H_NH})$ 5.89			3.91(s) $J(\mathrm{PH_N}) \sim 2.7$ $J(\mathrm{H_NH})$ 5.89	
3b	6.66	5.87(d) $J(\mathrm{PH})$ 5.91	3.77	2.84	$\mathrm{H_A}$ 4.82(dd) $J(\mathrm{H_AH_B})$ 13.8 $J(\mathrm{H_NH_A})$ 5.29	$\mathrm{H_B}$ 3.70(dd) $J(\mathrm{H_AH_B})$ 13.8 $J(\mathrm{PH_B})$ 4.7	2.91(dd) $J(\mathrm{PH})$ 2.23 $J(\mathrm{H_NH})$ 6.15	4.20(br,q)	
3c	6.62	5.92(d) $J(\mathrm{PH})$ 6.01	3.76	2.88	$\mathrm{H_A}$ 4.45(d) $J(\mathrm{H_AH_B})$ 11.3	$\mathrm{H_B} \sim 3.80$[b]		~ 4.5	CH$_2$ 4.84(d) $J(\mathrm{H_NH})$ 13.7
3d	6.63	5.91(d) $J(\mathrm{P_H})$ 5.88	3.77	2.87	$\mathrm{H_A}$ 4.43(dd) $J(\mathrm{H_AH_B})$ 14.3 $J(\mathrm{H_NH_A})$5.0	$\mathrm{H_B} \sim 380$[b]		4.34(br)	CH$_2$ 4.77(d) $J(\mathrm{H_NH})$ 13.8 OMe 3.81
3e	6.60	5.92(d) $J(\mathrm{PH})$ 4.61	3.76	2.87	$\mathrm{H_A}$ 4.47(d) $J(\mathrm{H_AH_B})$ 11.1	$\mathrm{H_B} \sim 3.80$[b]		~ 4.5	CH$_2$ 4.78(d) $J(\mathrm{H_NH})$ 13.3 OMe 3.88, 3.85
3f	6.56	5.78 $J(\mathrm{PH})$ 6.26	3.75	2.84	$\mathrm{H_A}$ 4.70(dd) $J(\mathrm{H_AH_B})$ 14.6 $J(\mathrm{H_NH_A})$ 6.33	$\mathrm{H_B}$ 3.95(dd) $J(\mathrm{H_AH_B})$ 14.6 $J(\mathrm{PH_B})$ 4.50		4.43(t) $J(\mathrm{PH_N}) \sim 5.9$ $J(\mathrm{H_NH_A})$ 6.33	Bu^t 1.32

3g	6.55	5.83(d) J(PH) 5.47			4.21(br,t) $J(H_NH) \sim 6$			3.90(br)	5.64 (OCH_2O)
3h	6.63	5.79(d) J(PH) 5.71			H_A 4.77(dd) $J(H_AH_B)$ 13.7 $J(H_NH_A)$ 5.1	H_B 3.63(dd) $J(H_AH_B)$ 13.7 $J(PH_B)$ 4.5	2.85(dd) J(PH) 2.67 $J(H_NH)$ 6.01	4.23(br)	5.64 (OCH_2O)
3j	6.65(d)	6.19(q) J(PH) 5.70	3.61		H_A 4.78(dd) $J(H_AH_B)$ 13.9 $J(H_NH_A)$ 4.9	$H_B \sim 3.7$	2.85(dd) J(PH) 2.69 $J(H_N)$ 6.10	4.33(br,q)	H_5 6.01(d)
3l	[c]	[c]			H_A 4.84(dd) $J(H_AH_B)$ 13.6 $J(H_NH_A)$ 5.35	H_B 3.70 $J(PH_B)$ 5.48	2.86(dd) J(PH) 2.76 $J(H_NH)$ 6.25	4.28(br,q) $J(H_NH)$ 6.25	
4a	6.87	6.51	3.90	3.79	4.11(t) $J(H_NH)$ 5.79			3.66(br,t)	CH_3(acac) 1.93 CH(acac) 2.05 CH(acac) 5.33
4i	[c]	[c]	3.74		4.13(t) $J(H_NH)$ 5.78			3.71(br)	CH_3(acac) 1.92 CH_3(acac) 2.03 CH(acac) 5.31
4k	[c]	[c]			4.15(t) $J(H_NH)$ 5.94			3.70(br)	CH_3(acac) 1.93 CH_3(acac) 2.05 CH(acac) 5.32

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[a] d, doublet; t, triplet; q, quartet; dd, doublet of doublets; s, sextet; br, broad. [b] Concealed under OMe peak. [c] Not unequivocably assignable.

Analytical data for all of the new compounds prepared are summarised in Table 1, together with yields.

Results and discussion

The method described here for the preparation of cyclopalladated primary and secondary benzylamines is similar to that reported previously for the cyclopalladated benzalimines (see Scheme 1) [1]. A solution containing a 1.1/1 molar ratio of an *ortho*-bromo primary or secondary benzylamine and bis(dibenzylideneacetone)palladium(0) in sodium-dried benzene was heated slowly to 50–60°C when reaction became rapid, and the deep purple colour of the Pd^0 complex was discharged, with the formation of a precipitate. In the cases of the secondary benzylamines the precipitate was yellow or yellowish-green, whereas with the primary benzylamines it was a greyish colour. Almost all of these dimeric palladium complexes were insoluble in all of the solvents examined. However, di-μ-bromo-bis(*N*-methyl-3,4-dimethoxybenzylamine-6-*C*,*N*)dipalladium(II) (**2b**) was recrystallised from a large volume of chloroform, and satisfactory elemental analytical data were obtained (see Table 1), although a molecular weight could not be measured. The dimeric nature of these complexes can, therefore, only be inferred from the similarity of their properties with those of the cyclopalladated benzalimines [1] and the tertiary benzylamines [2,15]. It is noteworthy that *N*,*N*-dimethyl-3,4-dimethoxy-6-bromobenzylamine reacts with bis(benzylideneacetone)palladium(0) to yield di-μ-bromo-bis(*N*,*N*-dimethyl-3,4-dimethoxybenzylamine-6-*C*,*N*)dipalladium(II) which, with triphenylphosphine gives the corresponding known [15] monomeric triphenylphosphine complex. Physical data for these complexes agree with those already published. In the IR spectra of the dimeric complex of type **2**, NH stretching absorptions occur at about 3200 cm^{-1} (see Table 1). The complexes were fully characterised as the triphenylphosphine monomers of type **3**, or as the acetylacetonates **4**. When the dimeric complex **2f**, containing an *N*-butyl group, was treated with an excess of triphenylphosphine ($> 2/1$ molar ratio), a new complex, (**5f**), was produced, containing two triphenylphosphine groups. A similar compound, chloro-[ethyl-*N*-methyl-*N*-(3,4-methylenedioxy)benzylglycinate-6-*C*]-bis(triphenylphosphine)palladium(II) had been prepared previously [13]. The complex **5f** exhibits fluxional behaviour, and this will be described in detail in a separate publication.

The ^1H NMR spectra of the monomeric triphenylphosphine complexes **3** exhibited similar behaviour to those reported for the corresponding tertiary benzylamine [15] and benzalimine [1] complexes. In particular, the C(5)–H resonates at about δ 5.9, and appears as a doublet ($J(^1H-^{31}P) \simeq 6$ Hz) (see Table 2). The resonance due to a methoxyl group at C(4) is shifted upfield to about δ 2.8–2.9, thus showing that the PPh_3 ligand is *trans* to nitrogen, as shown in **3**. The hydrogen atoms of the CH_2 group in the chelate ring exhibit rather more complex patterns. Thus, in **3b**–**3f**, **3h**, **3j** and **3l**, an *AB* quartet is observed, the lower field part of which is further split by the NH group. The higher field part of the *AB* quartet is also further split into doublets by coupling to ^{31}P. The nature of these couplings was established by appropriate decoupling experiments. In **3a** the CH_2 group appeared as a pseudo sextet, which collapsed into a doublet, with residual ^{31}P coupling upon irradiating at the frequency of the NH_2 hydrogen absorption. Similarly, upon irradiation at the frequency of the CH_2 group absorption, the signals due to the

TABLE 3. ^{13}C NMR SPECTRAL DATA (δ in ppm)

Compound	δ(Ar)						δ(ArCH$_2$N)	δ(OMe)	Triphenylphosphine				Other
	1	2	3	4	5	6			C(1)	C(2,6)	C(3,5)	C(4)	
3a	~142	105.2	~145	144.3[a]	121.3 (~10)	146.1	53.9	55.8 55.1	131.5 (49.2)	135.4 (11.3)	128.1 (11.1)	130.8	
3b	142.6	106.4	145.9	144.9 (4.8)	121.0 (10.8)	142.6	63.0	55.8 55.0	131.5 (49.2)	135.3 (11.2)	128.1 (10.8)	130.7	CH$_3$ 40.1
3c	143.1	106.5	145.9	145.0[a]	120.9 (11.6)	142.0	57.3	55.9 55.0	131.5 (49.2)	135.3 (12.1)	128.2 (10.8)	130.8	Ph 136.6 CH$_2$ 54.3 129.4, 128.9, 128.2
3d	143.1	106.4	145.9	145.0[a]	120.9 (11.8)	142.0	57.0	55.9 55.3 55.0	131.5 (49.0)	135.3 (12.2)	128.2 (11.7)	130.7	Ph 159.5 CH$_2$ 53.7 128.7 114.3
3e	143.1	106.4	145.9	144.8[a]	120.9 (8.3)	142.1	57.3	56.0 56.0 55.8 55.0	131.5 (50.1)	135.3 (12.6)	128.2 (10.8)	130.7	Ph 149.4 121.8 CH$_2$ 54.3 149.0 112.4 129.2 112.2
3f	144.4	105.1	146.0	144.9 (6.5)	120.2 (10.8)	141.2	55.1	55.8 55.1	131.8 (48.9)	135.3 (12.2)	128.1 (9.9)	130.7	58.7 $C(CH_3)_3$ 30.8 $C(CH_3)_3$
3g	[b]	102.5	144.6[c]	144.3[c]	117.2 (10.8)	144.0[c]	54.0		130.9 (40.1)	135.4 (12.2)	128.2 (10.8)	130.8	OCH$_2$O 100.1
3h	144.1	103.7	144.5	143.8 (7.3)	117.9 (11.6)	142.6	63.0		131.3 (50.5)	135.3 (11.5)	128.1 (11.7)	130.7	OCH$_2$O 100.0 CH$_3$ 39.8
3j	142.3	109.1	151.8	110.2 (4.4)	138.0 (9.9)	156.7	63.0	55.0	131.6 (50.2)	135.3 (12.2)	128.0 (11.5)	130.6	CH$_3$ 40.0
4k	145.2[c]	125.0[c]	124.5[c]	120.3[c]	131.1[c]	150.2[c]	53.1						CO 187.4 CH(acac) 100.2 CO 187.2 2CH$_3$(acac) 27.8
3l	150.8[c]	122.8[c]	124.0[c]	124.9 (4.6)	137.6 (10.6)	152.5[c]	63.0		131.5 (49.1)	135.3 (12.2)	128.0 (10.7)	130.6	CH$_3$ 40.0
4a	135.5	105.0	147.1	145.9	113.6	141.3	52.9	56.3 55.9					CO 187.5 CH(acac) 100.1 187.0 2CH$_3$(acac) 27.8
4i	134.7	106.8	150.5	110.7	131.4	157.7	53.0	55.3					CO 187.3 CH(acac) 100.2 2CH$_3$(acac) 27.8

[a] Peak broadened due to P coupling. [b] Under triphenylphosphine resonances. [c] Assignment uncertain.

NH_2 group collapsed to a doublet with residual ^{31}P coupling ($J(^1H-^{31}P) \simeq 2.7$ Hz). In the acetylacetonate derivatives **4i** and **4k**, the CH_2 group of the chelate ring resonates as a triplet with $^1H-^1H$ coupling to the NH_2 group ($J \simeq 6$ Hz).

The ^{13}C NMR spectra of the monomeric triphenylphosphine complexes of type **3** were assigned as fully as possible (Table 3) using FD and SFORD techniques. In the complexes **3a–3h**, **3j** and **3l** the six aromatic ring carbon atoms of the cyclopalladated system were identified, but unequivocable assignments could not be made, especially with **3g** and **3l**. Assignments were based upon the previous work of Barr and Dyke [16]. The absorption due to the CH_2 group of the chelate ring occurred at 57–64 ppm in the secondary amine complexes, and at about 53 ppm in the primary amine complexes. In the acetylacetonate complexes the two $>C=O$ groups resonated at about 187 ppm, the methine carbon at about 160 ppm and in all cases the two methyl group carbons were coincidentally equivalent at 27.8 ppm.

The chemistry, and in particular, the insertion reactions of these cyclopalladated primary and secondary benzylamines is under investigation and will be described later.

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