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The cyclopalladation of benzylidenebenzylamines

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Abstract

A number of isomeric *N*-benzylbenzalimine palladium(II) complexes of the type $[PdX(o\text{-}C_6H_4 \cdot C(CH_3)=N \cdot CH_2Ph]_2$ (with C=N *endo* to the palladocycle) and $[PdX(o\text{-}C_6H_4 \cdot CH_2N=C(CH_3Ph]_2$ (with C=N *exo* to the palladocycle), have been prepared and characterised by ^1H and ^{13}C NMR methods. The crystal structures of two analogous monomeric acac complexes, synthesized independently by oxidative addition of $o\text{-}BrC_6H_4CH_2N=CH \cdot Ph$ to Pd(dibenzylideneacetone)$_2$ have also been determined. These are $[Pd(acac)(o\text{-}C_6H_4 \cdot CH=N \cdot CH_2Ph)]$ (**15a**) and $[Pd(acac)(o\text{-}C_6H_4 \cdot CH_2N=CHPh)]$ (**20a**). Crystals of **15a** are monoclinic, space group $P2_1/a$ with $Z = 4$ in a cell of dimensions a 10.286(2), b 11.902(3), c 13.895(5) Å, β 93.52(2)° while **20a** is monoclinic, space group $P2_1/c$ with $Z = 8$ and a 10.353(3), b 20.600(5), c 16.545(7) Å, β 92.14(3)°. The structures **15a** and **20a** were refined to residuals $R = 0.041$ and 0.055 for 1661 and 2525 observed reflections respectively.

Introduction

Cyclometallation of nitrogen-containing ligands with transition metal complexes is a rapidly growing area of organometallic chemistry [1–3]. In particular, cyclopalladation of tertiary benzylamines, benzalimines and aromatic azo compounds has attracted attention because "insertion" of certain types of alkenes into the aromatic carbon–palladium bond has proved to be facile, leading to metal-free compounds with some potential in organic synthesis [4–12].

Cope and Friedrich [13] proposed that the cyclopalladation of tertiary benzylamines involves initial, rapid coordination of the palladium with the nitrogen atom, followed by electrophilic attack of the metal on the *ortho*-position of the benzene ring. Subsequently it became generally accepted that cyclopalladation of azobenzenes also involves a similar mechanism, and this concept has been extended to

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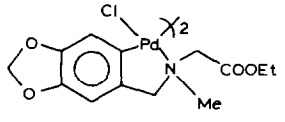
benzalimines [2,14–16]. It has been suggested [17] that complexes in which a ligand proton makes a close approach to the metal centre may be intermediates during such reactions, and some ^{1}H NMR evidence, in the case of benzylamines, has [18] been presented to support this concept.

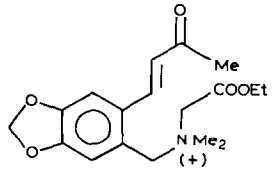
Under normal conditions [13], only tertiary benzylamines undergo cyclopalladation; primary and secondary benzylamines yield complexes of the type $(ArCH_2NHR)_2PdCl_2$ (where R = H or alkyl). However, cyclic complexes may be prepared readily from all three types of benzylamines by treating the corresponding *ortho*-bromobenzylamine derivative with bis(dibenzylideneacetone)palladium(0) [$Pd(dba)_2$] [19]. The same reaction conditions can be used [20] with advantage in the preparation of bromo(*N*-substitutedbenzalimine-6,*C*,*N*)triphenylphosphinepalladium(II) complexes because oxidative addition of $Pd(dba)_2$ to the aromatic carbon–bromine bond is regiospecific, whereas cyclopalladation of the benzalimine can give rise to some ambiguity [21].

In previous work [4,5], attempts to utilise insertion reactions of cyclopalladated tertiary benzylamines to synthesise nitrogen heterocyclic compounds have been described. The limited success was due, in part, to the fact that cyclisations of compounds such as **2** (easily obtained by insertion of methyl vinyl ketone into the carbon–palladium bond of **1**, followed by methylation) gave quaternary salts (such as **3**) which were very difficult to purify. Unfortunately, except for reactions with carbon monoxide, insertion reactions involving cyclopalladated primary and secondary benzylamines have failed so far. Michael addition products of the type **4** are formed instead.

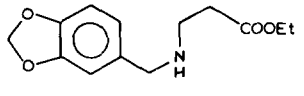
Onoue and Moritani [22] showed that benzalimines, regarded as masked aldehydes and ketones, undergo cyclopalladation with palladium acetate in acetic acid with a ligand/metal ratio of approximately 1/1 to give good yields of the acetate-bridged dimers. However, they were unable to repeat the work of Molnar and Orchin [23] who reacted the ligands with $(PhCN)_2PdCl_2$ under conditions which were later shown [24] to lead to rapid hydrolysis of the imine. Some of these acetate bridged dimers have been found [25] to react with Grignard reagents which, after hydrolysis, led to *ortho*-alkylbenzaldehydes. Girling and Widdowson [10,26] have also reported some cyclopalladated benzalimines and subsequent insertion of elec-



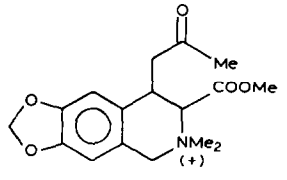
(1)



(2)

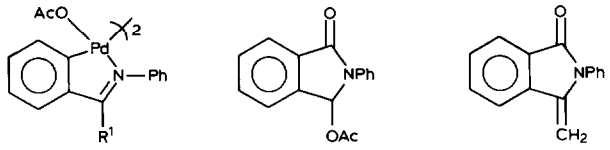


(4)



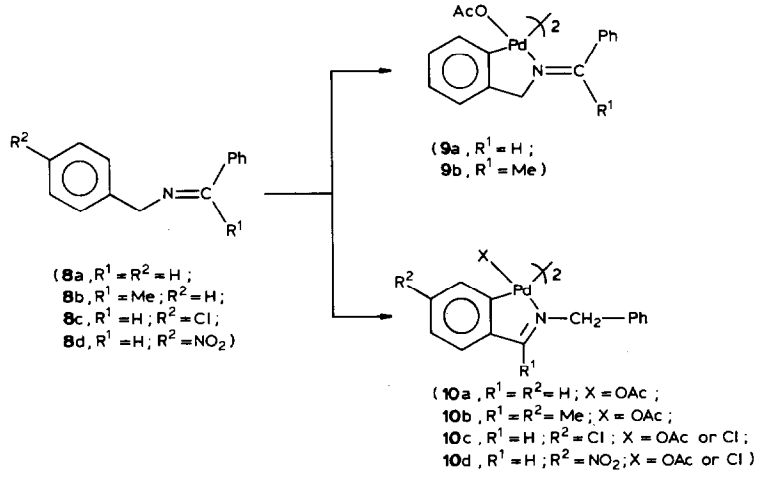
(3)

tron-poor alkenes. Thompson and Heck [7] described the reactions of carbon monoxide with the bridged acetate dimers (**5**, $R^1 = H$) and (**5**, $R^1 = Me$). Amongst other products they isolated **6** from the former and **7** from the latter complex.



(5) (6) (7)

Thompson and Heck [7] also described the cyclopalladation of the imines **8a** and **8b** with palladium acetate. Although it was recognised [27] that the products may be **9a** and **9b** or **10a** and **10b** respectively, the authors decided that cyclopalladation had "...occurred, as expected, on the more activated benzyl ring"; the assignments of structures as **9a** and **9b** were, in the view of the authors, supported by the presence of an AB quartet in the ^1H NMR spectra, centred at 3.2 δ and assigned to the CH_2 group in the five-membered ring.



(**8a**, $R^1 = R^2 = H$; **8b**, $R^1 = Me$; $R^2 = H$; **8c**, $R^1 = H$; $R^2 = Cl$; **8d**, $R^1 = H$; $R^2 = NO_2$)

(**9a**, $R^1 = H$; **9b**, $R^1 = Me$)

(**10a**, $R^1 = R^2 = H$; X = OAc; **10b**, $R^1 = R^2 = Me$; X = OAc; **10c**, $R^1 = H$; $R^2 = Cl$; X = OAc or Cl; **10d**, $R^1 = H$; $R^2 = NO_2$; X = OAc or Cl)

(11) (12)

Although *syn* and *anti* isomers are possible, it seemed from the ^1H NMR spectra that only one isomer was present, and, as shown in **9**, this was presumed to be the *anti* isomer. Reaction of these complexes with CO then gave products formulated [7] as **11** from **9a** and **12** from **9b**.

In 1984 Albert et al. [28] repeated the cyclopalladation of **8a**, and also cyclopalladated the *p*-chloro and *p*-nitro derivatives **8c** and **8d**, respectively, using either palladium chloride or palladium acetate. The products were characterised as the bis-triethylphosphine derivatives, or as the monotriphenylphosphine compound of type **14**. From an examination of the ^1H NMR spectra, especially from **8c** and **8d**,

they concluded that palladation had given the endocyclic imine derivatives **10a**, **10b** or **10d** (X = OAc or Cl).

We also were interested in complexes of the type **9**, hoping that insertion of electron-poor alkenes, followed by hydrolysis, would yield *o*-styrylbenzaldehydes which might be elaborated further to nitrogen heterocycles. We have confirmed that cyclopalladation of **8a** and **8b** give **10a** and **10b**, respectively. We have also found that even for those imines in which the "activated" benzyl ring carries "activating", electron donor substituents, cyclopalladation still occurs in the alternative benzal ring, rather than in the benzyl ring. Our conclusions are based upon extensive ^{1}H NMR (300 MHz) and ^{13}C NMR spectral data, alternative syntheses of both series **9** and series **10** compounds and X-ray structural analysis of them.

Experimental

Preparation of complexes

The benzalimines and the cyclic palladium complexes (see Supplementary Table I), were prepared as described previously [4,20,29,30] and ^{1}H and ^{13}C NMR spectral data and GC-MS data were obtained as before [20,30]. Microanalyses and molecular weight determinations were performed by the Australian Microanalytical Service, Melbourne.

Table 1

Cell data and details of the data collection for compounds **15a** and **20a** at 20 °C

	15a	**20a**
Mol. formula	$C_{19}H_{19}NO_2Pd$	$C_{19}H_{19}NO_2Pd$
FW	399.6	399.6
a	10.286(2) Å [a]	10.353(3) Å
b	11.902(3) Å	20.600(5) Å
c	13.895(5) Å	16.545(7) Å
β	93.52(2)°	92.14(3)°
V	1697.9 Å^3	3526.2 Å^3
Z	4	8
d_{calc}	1.560 g cm^{-3}	1.500 g cm^{-3}
d_{obs}	1.55 g cm^{-3}	1.51 g cm^{-3}
λ(Mo-K_α)	0.71069 Å	0.71069 Å
μ(Mo-K_α)	10.8 cm^{-1}	10.4 cm^{-1}
F(000)	808	1616
Crystal class	monoclinic	monoclinic
Space group	$P2_1/a$ [b]	$P2_1/c$
Absences	$h0l$, h = odd; $0k0$, k = odd	$h0l$, l = odd; $0k0$, k = odd
Crystal size	0.33×0.12×0.12 mm	0.20×0.20×0.12 mm
Colln. range	2θ, 3–45°; hkl, 11, 8, ±13	2θ, 3–45° C; hkl, 12, 23, ±18
Scan type	θ-2θ	$\theta-2\theta$
Standards	(8,0,0); (0,8,0); (0,0,12)	(6,0,0); (0,10,0); (0,0,8)
Max./min trans. factors	0.892, 0.857	0.882, 0.794
Unique reflections, R_{merg}	1972, 0.016	3282, 0.021
Observed reflections	1661 [$I > 2.5\sigma(I)$]	2525 [$I > 2.5\sigma(I)$]

[a] Standard cell: $P2_1/c$: a 13.895(5), b 11.902(3), c 10.286(2) Å, β 93.52(2)°. [b] Symmetry operations: $\pm(x, y, z), \pm(\frac{1}{2}+x, \frac{1}{2}-y, z)$.

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å^2, $\times 10^3$) for compounds **15a** and **20a**. U_{eq} is defined as $(U_{11} \cdot U_{22} \cdot U_{33})^{1/3}$

Compound **15a**				
Atom	x/a	y/b	z/c	U_{eq}
Pd	8062.5(5)	3132.3(4)	1981.8(3)	36.9(4)
O(1)	7831(5)	1404(4)	1772(4)	50(3)
C(1)	7030(6)	985(6)	1148(5)	43(4)
C(2)	6119(7)	1583(6)	565(5)	50(5)
C(3)	5907(6)	2734(6)	548(5)	44(4)
O(3)	6545(5)	3475(4)	1052(3)	47(3)
C(11)	7083(8)	−267(6)	1038(6)	61(5)
C(31)	4832(7)	3226(6)	−128(6)	54(5)
C(1A)	8455(8)	4712(6)	2207(6)	42(5)
C(2A)	9592(8)	4893(7)	2805(6)	48(5)
C(3A)	10043(9)	5964(8)	3045(6)	58(6)
C(4A)	9353(10)	6872(7)	2687(7)	62(6)
C(5A)	8210(10)	6713(8)	2112(7)	60(7)
C(6A)	7798(9)	5650(7)	1871(6)	54(6)
C(21)	10208(6)	3857(6)	3154(7)	48(4)
N(21)	9640(5)	2943(5)	2894(4)	41(4)
C(211)	10130(7)	1850(6)	3233(6)	48(4)
C(1B)	9248(7)	1306(6)	3911(5)	36(5)
C(2B)	9007(8)	190(10)	3822(7)	62(6)
C(3B)	8233(9)	−381(8)	4513(8)	68(6)
C(4B)	7776(9)	210(10)	5218(9)	72(7)
C(5B)	8008(10)	1395(10)	5325(7)	77(7)
C(6B)	8760(9)	1904(8)	4659(6)	58(6)
Compound **20a**				
	Molecule A			
Atom	x/a	y/b	z/c	U_{eq}
Pd	5367.9(9)	6907.8(5)	5519.4(5)	59.0(6)
O(1)	6887(9)	7572(4)	5665(2)	74(6)
C(1)	7945(13)	7452(9)	6000(8)	76(11)
C(2)	8363(13)	6867(8)	6276(8)	83(11)
C(3)	7651(13)	6292(8)	6230(7)	91(11)
O(3)	6506(8)	6192(4)	5941(5)	91(6)
C(11)	8840(14)	8023(9)	6104(9)	114(12)
C(31)	8256(18)	5695(7)	6570(7)	167(16)
C(1A)	3894(12)	6321(7)	5466(7)	64(9)
C(2A)	2682(15)	6623(7)	5368(7)	69(10)
C(3A)	1537(15)	6269(9)	5337(8)	91(12)
C(4A)	1657(17)	5591(10)	5375(10)	112(14)
C(5A)	2828(21)	5297(8)	5474(9)	106(13)
C(6A)	3977(14)	5634(8)	5493(8)	81(11)
C(21)	2661(12)	7358(7)	5349(7)	72(9)
N(21)	3970(9)	7564(5)	5151(5)	59(6)
C(211)	4046(12)	8119(6)	4813(7)	72(8)
C(1B)	5208(12)	8409(7)	4471(7)	68(9)
C(2B)	6110(13)	8042(6)	4071(7)	73(9)
C(3B)	7188(14)	8307(8)	3672(9)	103(12)
C(4B)	7245(16)	8992(10)	3727(10)	111(14)
C(5B)	6367(16)	9394(9)	4134(12)	121(15)
C(6B)	5290(14)	9088(7)	4474(10)	110(12)

continued

Table 2 (continuation)

Compound **20a**				
	Molecule B			
Atom	x/a	y/b	z/c	U_{eq}
Pd	1547.4(9)	7529.9(4)	2958.5(5)	55.6(6)
O(1)	1667(7)	6688(3)	2266(4)	66(5)
C(1)	965(12)	6204(5)	2359(8)	65(9)
C(2)	−11(14)	6148(6)	2901(8)	81(10)
C(3)	−500(13)	6655(6)	3373(7)	69(9)
O(3)	−81(8)	7222(4)	3454(5)	72(6)
C(11)	1252(14)	5615(6)	1834(8)	95(10)
C(31)	−1643(14)	6531(7)	3909(9)	112(12)
C(1A)	1469(12)	8389(5)	3469(7)	57(8)
C(2A)	2274(12)	8835(5)	3150(7)	60(8)
C(3A)	2291(13)	9461(6)	3456(8)	78(10)
C(4A)	1514(16)	9639(7)	4076(9)	90(11)
C(5A)	666(14)	9187(7)	4404(9)	84(11)
C(6A)	625(11)	8566(6)	4087(7)	65(8)
C(21)	3127(12)	8638(5)	2500(7)	79(9)
N(21)	3216(9)	7906(4)	2585(5)	56(6)
C(211)	4294(13)	7634(5)	2453(6)	55(8)
C(1B)	4535(10)	6937(5)	2566(6)	60(7)
C(2B)	5344(13)	6637(7)	2012(7)	87(10)
C(3B)	5615(16)	5949(8)	2107(10)	117(14)
C(4B)	5164(15)	5603(7)	2763(9)	102(12)
C(5B)	4422(13)	5931(6)	3322(7)	73(9)
C(6B)	4100(11)	6584(6)	3230(6)	63(8)

X-Ray structure analysis

Suitable crystals of the isomeric compounds **15a** and **20a** were grown from chloroform and methylene chloride/methanol respectively as yellow prisms. Single crystal specimens were used for data collection on a Nicolet R3m four-cycle diffractometer, using graphite-monochromatized Mo-K_α radiation. Accurate cell parameters were obtained from least-squares refinement of 15 high-angle reflections. No crystal decomposition was in evidence in either compound from the intensities of three standards regularly monitored throughout the data collection period. Data were corrected for Lorentz and polarization effects and absorption but not for extinction. Cell data and details of the data collection for compounds **15a** and **20a** are given in Table 1.

The positions of the palladium atoms in **15a** and **20a** were located using three-dimensional Patterson syntheses. The remaining non-hydrogens were found by weighted difference-Fourier methods. Block-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms gave final residuals $R[=\Sigma|\,|F_o|-|F_c|\,|/|\Sigma|F_o|\,|]=0.041$ (**15a**) and 0.055 (**20a**) and $R_w[=(\Sigma w|\,|F_o|-|F_c|\,|^2/\Sigma w|\,|F_o|\,|^2)^{1/2}]=0.048$ (**15a**) and 0.055 (**20a**). Weighting schemes were $w=1.0/(\sigma^2F_o+3.1\times10^{-3}\,F_o^2)$ (**15a**) and $1.3(\sigma^2F_o+6.8\times10^{-4}\,F_o^2)$ (**20a**). Hydrogen atoms were located by difference methods and included in the refinements at fixed positions with their isotropic temperature factors set invariant at 0.05 Å^2. All computations were completed using the SHELX-76 [31] program set on a DEC

Table 3

Bond distances (Å) and angles (°) for compounds **15a** and **20a**

	15a	**20a**	
		A	B
Pd(1)–C(1)A	1.955(7)	1.946(9)	1.964(10)
Pd(1)–N(21)	2.008(5)	2.056(9)	2.012(10)
Pd(1)–O(1)	2.078(5)	2.091(7)	2.084(7)
Pd(1)–O(3)	2.008(5)	1.997(8)	2.005(8)
C(1A)–C(2A)	1.41(1)	1.40(2)	1.36(2)
C(1A)–C(6A)	1.37(1)	1.42(2)	1.42(2)
C(2A)–C(3A)	1.39(1)	1.39(2)	1.38(2)
C(3A)–C(4A)	1.37(1)	1.40(2)	1.38(2)
C(4A)–C(5A)	1.39(1)	1.36(2)	1.40(2)
C(5A)–C(6A)	1.37(1)	1.38(2)	1.38(2)
C(2A)–C(21)	1.45(1)	1.51(2)	1.47(2)
C(21)–N(21)	1.28(1)	1.47(1)	1.52(1)
N(21)–C(211)	1.46(1)	1.28(1)	1.28(2)
C(211)–C(1B)	1.50(1)	1.47(2)	1.47(1)
C(1B)–C(2B)	1.36(1)	1.39(2)	1.41(2)
C(1B)–C(6B)	1.38(1)	1.40(2)	1.40(2)
C(2B)–C(3B)	1.45(1)	1.43(2)	1.45(2)
C(3B)–C(4B)	1.32(1)	1.41(3)	1.39(2)
C(4B)–C(5B)	1.44(1)	1.42(3)	1.40(2)
C(5B)–C(6B)	1.38(1)	1.41(2)	1.39(2)
C(1)–O(1)	1.26(1)	1.23(2)	1.25(1)
C(1)–C(11)	1.50(1)	1.50(2)	1.53(2)
C(1)–C(2)	1.40(1)	1.35(2)	1.38(2)
C(2)–C(3)	1.39(1)	1.40(2)	1.41(2)
C(3)–O(3)	1.28(1)	1.28(2)	1.25(1)
C(3)–C(31)	1.52(1)	1.48(2)	1.53(2)
C(1)A–Pd–N(21)	81.4(3)	81.5(3)	80.5(4)
C(1)A–Pd–O(1)	174.6(3)	175.1(4)	172.0(4)
C(1)A–Pd–O(3)	92.7(3)	90.5(3)	93.5(4)
N(21)–Pd–O(1)	93.7(2)	97.0(3)	94.7(3)
N(21)–Pd–O(3)	173.9(2)	171.3(4)	172.9(3)
O(1)–Pd–O(3)	92.1(2)	90.6(3)	91.7(3)
Pd–C(1A)–C(2A)	113.5(2)	115.2(9)	114.0(8)
Pd–C(1A)–C(6A)	129.8(6)	124.9(8)	125.3(8)
Pd–N(21)–C(21)	115.2(5)	112.9(8)	111.7(7)
Pd–N(21)–C(211)	123.2(4)	131.6(8)	130.6(8)
Pd–O(1)–C(1)	123.4(4)	124.6(8)	123.4(8)
Pd–O(3)–C(3)	124.0(4)	122.6(8)	123.1(8)
C(2A)–C(1A)–C(6A)	116.7(4)	120(1)	121(1)
C(1A)–C(2A)–C(3A)	122.3(7)	122(1)	119(1)
C(1A)–C(2A)–C(21)	113.3(8)	117(1)	119(1)
C(3A)–C(2A)–C(21)	124.4(7)	121(1)	122(1)
C(2A)–C(3A)–C(4A)	118.6(8)	117(1)	121(1)
C(3A)–C(4A)–C(5A)	120.0(8)	122(1)	120(1)
C(4A)–C(5A)–C(6A)	120.2(9)	123(1)	119(1)
C(5A)–C(6A)–C(1A)	122.0(8)	117(1)	120(1)
C(2A)–C(21)–N(21)	116.5(6)	106(1)	104(1)
C(21)–N(21)–C(211)	121.6(6)	115(1)	118(1)
N(21)–C(211)–C(1B)	112.2(6)	126(1)	124(1)
C(211)–C(1B)–C(2B)	118.8(7)	117(1)	117(1)
C(211)–C(1B)–C(6B)	121.0(7)	122(1)	123(1)
C(2B)–C(1B)–C(6B)	120.1(8)	120(1)	120(1)

continued

Table 3 (continuation)

	15a	20a	
		A	B
C(1B)–C(2B)–C(3B)	120.2(9)	124(1)	118(1)
C(2B)–C(3B)–C(4B)	118.4(10)	113(1)	121(1)
C(3B)–C(4B)–C(5B)	122.5(11)	126(2)	118(1)
C(4B)–C(5B)–C(6B)	117.2(10)	126(2)	122(2)
C(5B)–C(6B)–C(1B)	121.5(9)	119(2)	120(2)
O(1)–C(1)–C(2)	125.7(6)	127(1)	126(1)
O(1)–C(1)–C(11)	115.9(6)	115(1)	116(1)
C(2)–C(1)–C(11)	118.4(6)	118(1)	118(1)
C(1)–C(2)–C(3)	127.8(6)	125(1)	125(1)
C(2)–C(3)–C(31)	119.9(6)	118(1)	120(1)
C(2)–C(3)–O(3)	126.5(6)	130(1)	128(1)
O(3)–C(3)–C(31)	113.6(6)	112(1)	112(1)

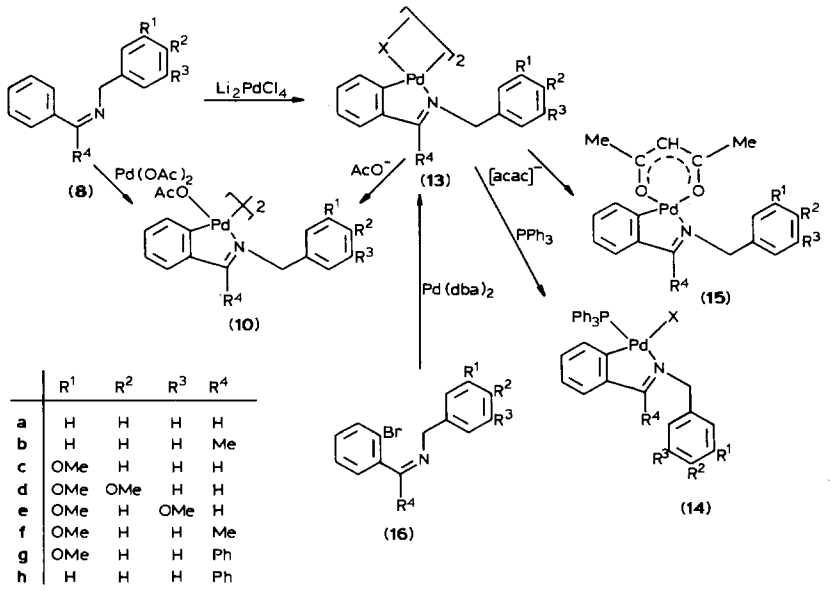
SYSTEM-10 computer. Atomic scattering factors and the f', f'' terms for anomalous dispersion were taken from ref. 32. Final atomic coordinates and equivalent isotropic thermal parameters are given in Table 2 while bond distances and angles are listed in Table 3. Anisotropic thermal parameters, hydrogen atom coordinates and structure factor tables are available from the authors (Supplementary Tables III and IV).

Results and discussion

A series of benzylbenzalimines (**8**) was treated with Li_2PdCl_4 in a 1/1 ratio (Scheme 1) to provide fair to good yields of the cyclopalladated compounds (Supplementary Table I). If the ratio of ligand/palladium salt was about 2/1, extensive hydrolysis occurred so that the only complex isolated was of the (benzylamine)$_2PdCl_2$ type. Chloro-bridged dimers **13** (X = Cl) isolated were, not unexpectedly [20,30], insoluble in the usual solvents so they were difficult to characterise. However, the complex **13a** derived from **8a** was crystallised from a large volume of chloroform and satisfactory analytical data were obtained. A ^1H NMR spectrum showed a broad resonance at 4.91δ, assigned to the CH_2 group present, and a peak at 7.68δ due to the C=NH proton. It was not possible to obtain a ^{13}C NMR spectrum for this compound. For ease of characterisation, these bridged dichlorides were converted into monomeric complexes **14** by reaction with triphenylphosphine, with the sodium salt of acetylacetone [Na^+ (acac)$^-$] (**15**) or were transformed into the bridged acetate dimers **10** (especially that derived from **8a**) with sodium acetate (Scheme 1).That cyclopalladation had occurred to give complexes of the types **10**, **13**, **14** and **15** was shown in three ways: (a) from ^1H and ^{13}C NMR spectral data; (b) by independent syntheses; and (c) from X-ray crystallographic data from compounds **15a** and **20a**.

(a) Spectral data

In the ^1H NMR spectra of the monomeric triphenylphosphine complexes **14a**, **14c–14e** (X = Cl) the resonance at ca. 5.2δ (which exhibited little or no coupling to



	R^1	R^2	R^3	R^4
a	H	H	H	H
b	H	H	H	Me
c	OMe	H	H	H
d	OMe	OMe	H	H
e	OMe	H	OMe	H
f	OMe	H	H	Me
g	OMe	H	H	Ph
h	H	H	H	Ph

Scheme 1

phosphorus) was assigned to the methylene group, while the absorption at ca. 7.9δ (with $J(PH) \simeq 6$ Hz in some cases) was assigned to the imine proton (CH=N). In the ^{13}C NMR spectra of these complexes **14a**, **14c–14e** (X = Cl) the peaks at ca. 158, 175 and 61 ppm were assigned to the Pd-C, C=N and ring methylene group resonances, respectively. These correlations are consistent with those reported by us for similar compounds [20]. Similarly, the resonances in the acetylacetonato complexes **15a–15i** at ca. 7.8, 4.8, 5.3 and 2.0δ in the ^1H NMR spectra were assigned to the CH=N, $-CH_2-$ (chelate ring), methine (acac residue) and methyl (acac residue) protons, respectively. In the ^{13}C NMR spectra of these same complexes, absorptions at about 157, 175, 61, 187, 100 and 28 ppm were assigned to the Pd-C, CH=N, CH_2, C=O (acac residue), methine and methyl groups, respectively. For each complex it is clear from both the ^1H and ^{13}C NMR spectral data that the methyl groups of the acac moiety, although chemically different, are magentically almost equivalent.

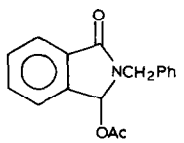
(b) Alternative syntheses

In order to synthesise complexes **9a** and **9b** unequivocally a series of *ortho*-brominated ligands **16** was prepared, and then utilised in the oxidative addition reaction described earlier [20,29] (Scheme 1). The reaction of **16a–16f** and **16h** with $Pd(dba)_2$ resulted in a series of dimeric, bridged bromocyclopalladated benzalimines **13a–13h** (X = Br). One of these, **13c** (X = Br) was sufficiently soluble for NMR spectral data to be collected. It exhibited resonances at ca. 4.9 and 7.7δ in the ^1H NMR spectrum corresponding to the methylene and imine protons, respectively. The ^{13}C NMR spectral data are consistent with the cyclopalladated structure. The dimeric complexes **13** were converted into the dimeric bridged acetates **10**, the monomeric bromo triphenylphosphine complexes **14** (X = Br), and the monomeric

acetylacetonato complexes **15** by standard methods; these derivatives were found to be identical with those obtained via the cyclopalladation reactions described above. As a further check, some of the chloro triphenylphosphine complexes **14a–14e** (X = Cl) were converted into the corresponding bromo complexes by metathetical reactions with lithium bromide.

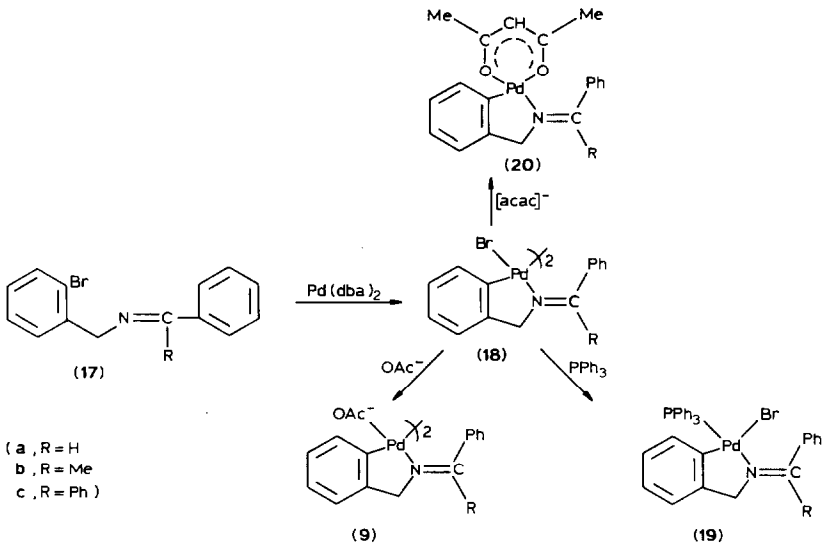
Furthermore, the cyclopalladation reaction of **8a** with palladium acetate, described by Thompson and Heck [7] was repeated, and the product described by them was obtained, but was found to be identical with **10a**, the compound produced either by cyclopalladation with Li_2PdCl_4, or by the oxidative addition of $Pd(dba)_2$ to **16a**, followed by reaction with sodium acetate. In the ^1H NMR spectrum, the protons of the methylene group appear as an AB quartet in agreement with Thompson and Heck. In addition there was further coupling (J 1.5 Hz) from the ^{31}P atom; the imine proton was also present as a triplet (J 1.5 Hz). Curiously, of all of the complexes of types **10**, **13** and **14** studied, the compound **10a** was the only one that exhibited an AB quartet for the methylene group, even though, in every case, these two hydrogen atoms are magnetically non-equivalent. The ^{13}C NMR spectrum of **10a**, which has now been recorded for the first time, contains distinct signals at 155.5δ (Pd-C), 171.9δ (N=C) and 61.5δ (CH_2) for the cyclometallated ligand, and at 181.4δ (C=O) and 24.5δ (CH_3) for the bridged acetate moiety.

The reaction of the cyclopalladated compound **10a** with carbon monoxide was repeated using Thompson and Heck's conditions, and the same products were obtained. In the ^{13}C NMR spectrum of the phthalimidine produced (and assigned structure **11** by Thompson and Heck), resonances are apparent at 44.3 (CH_2), 20.6 (CH_3), 170.8 and 167.7 (C=O) and 80.9 (CH) ppm. The signal at 167.7 was assigned to the ring-carbonyl group in the light of other work by us [30]. Consequently, we believe that the structure of this phthalimidine may be better represented as **24** rather than as **11**. This type of structure is consistent with the products for carbon monoxide insertion reactions described by Thompson and Heck [7].



(24)

In another series of experiments, *o*-bromophenylbenzalimines of type **17**, isomeric with **16**, were subjected to oxidative addition reactions with $Pd(dba)_2$ (Scheme 2). The dimeric-bridged dibromide complexes **18a–18c** that were formed, were converted into the bridged diacetates of type **9**, the monomeric bromotriphenylphosphine complexes **19** and the acetylacetonato complexes **20**. Some difficulty was experienced with these conversions. Thus, whereas the use of sodium acetate resulted in poor yields of impure product, of type **9**, good results were obtained with silver acetate. The triphenylphosphine complexes **19** were difficult to crystallise, and for these and the bridged acetates, NMR spectral data indicate that two isomeric species are present. In the triphenylphosphine complexes this is possibly due to a mixture where the Br ligand is either *cis* or *trans* to the nitrogen, although the evidence is ambiguous. The reactions of the complexes **18a–18c** with $Na^+[acac]^-$ gave pure, single isomeric forms of the expected complexes.



Scheme 2

(c) X-Ray structures

Crystal structures of the two acetylacetonato complexes **15a** and **20a** have been determined. These confirm the *endo-* and the *exo*-arrangements of the double bond in the benzylbenzamine moieties for complexes **15a** and **20a** respectively (Figs. 1 and 2). For **20a** there are two independent but similar monomer molecules in the asymmetric unit and these are essentially the same (Fig. 2 depicts molecule A;

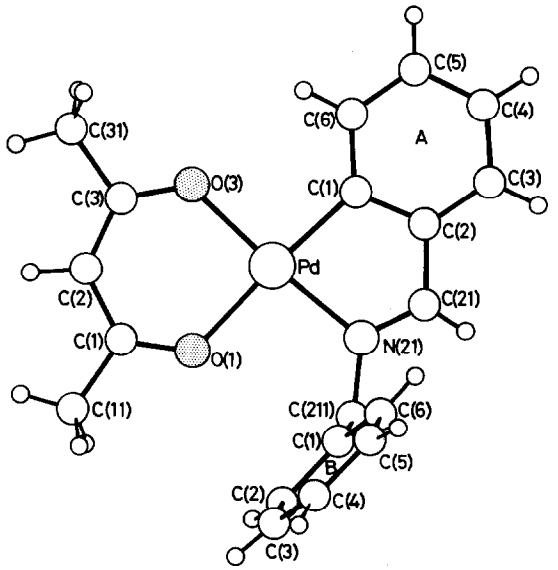


Fig. 1. Molecular configuration and atom naming scheme for compound **15a**. Hydrogens take the number of the parent carbon.

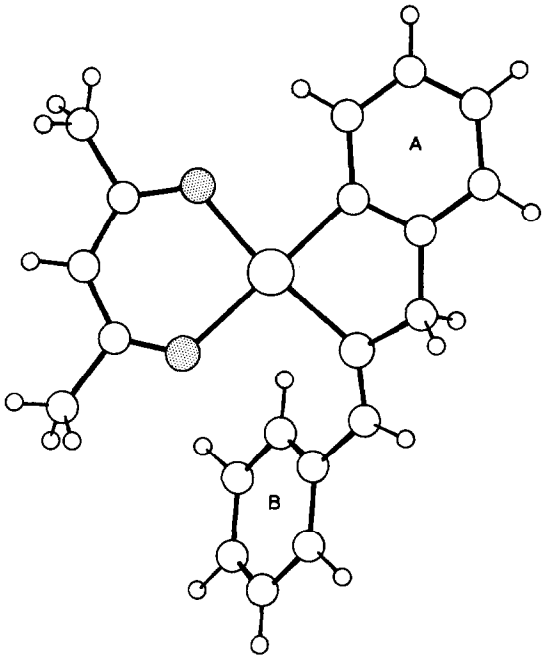
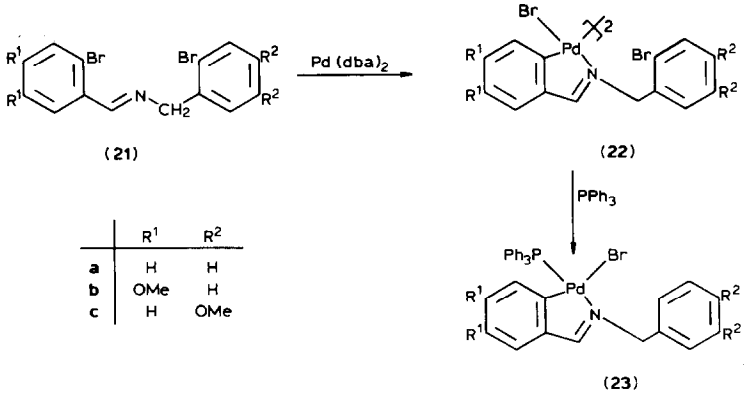


Fig. 2. Molecular configuration for compound **20a** (molecule A). Atom naming follows the convention of Fig. 1.

comparative torsion angles are found in Supplementary Table II). The molecular volume of **20a** (441 Å^3) is significantly greater than that for **15a** (424 Å^3). Therefore it is reasonable to assume that the *exo*-double bond in **20a**, with its greater stereochemical constraints, exerts an influence on the packing of the molecules in the cell. No unusually short intermolecular associations are found for either of the isomers, which is the situation expected in the packing of such molecules in the solid state.

Both complexes are discretely monomeric with the stereochemistry about Pd^{II} essentially square planar. The bond distances to Pd within the chelate rings show little variation between **15a** and **20a**. The values for Pd–C (1.955(7) and 1.95(1) Å (mean) respectively) and Pd–N (2.008(5) and 2.03(1) Å mean respectively) are comparable with the distances in the analogous complex, di-μ-chlorobis[*N*-(phenylamino)-α-phenylbenzylidenimino-2,*C*,*N*]dipalladium(II) [33] (Pd–C 1.967(3), Pd–N 2.027(4) Å). This complex has the same *endo* double bond as **15a** but is a bis-chloro-bridged dimer molecule. The Pd–C and Pd–N bond lengths in the three isomeric bis-chloro-bridged *N*,*N*-dimethylbenzylidene dimers (Pd–N, 2.075(4) Å (*ortho*); 2.069(3) Å (*meta*); 2.070(5) Å (*para*) and Pd–C, 1.976(4) Å (*ortho*); 1.986(3) Å (*meta*); 1.97(6) Å (*para*)) [34] are also similar. These examples reinforce the contention [33] that the Pd–C and Pd–N bond lengths are not significantly influenced by the presence of a double bond within the chelate ring. Of greater influence is the *trans*-effect upon the Pd–O bonds in the acac ligand. As expected [35], the bond *trans* to Pd–C is elongated relative to that *trans* to Pd–N in both **15a** (2.078(5), 2.008(5) Å) and **20a** (2.087(7), 2.001(8) Å (mean)). These values are



	R^1	R^2
a	H	H
b	OMe	H
c	H	OMe

Scheme 3

significantly greater than in bis(acetylacetonato)-palladium(II) (1.97(1) Å) [37]. In Pd(acac) complexes containing η^3-allylic ligands the Pd–O distances show similar elongation to those in **15a** and **20a**, e.g. π-cyclooctadienyl(acetylacetonato)palladium(II) (2.08(1) Å) [38].

In **20a**, the phenyl substituent of the benzylidine group has the *cis*-configuration (relative to Pd) about the N=C bond, and is therefore directed towards a methyl group of the acetylacetonato ligand. In keeping with this geometry, significant shifts of resonances due to CH_3 in both the ^1H and ^{13}C NMR spectra were observed. For example, in the ^1H NMR spectrum of **20a**, the resonance due to the methyl group is shifted 0.7 ppm upfield from its normal position. In addition, the imine proton in **20a** absorbs at 8.40δ, compared with 7.88δ in **15a**. In the ^{13}C NMR spectra, the resonances due to the methylene group in **20a–20c** are shifted upfield by about 14 ppm compared with the resonance positions of the corresponding carbon atoms in **15a**, **15b** and **15h**.

(d) Competitive cyclopalladation reactions

In order to compare the direction of cyclopalladation of benzalimines **8** using Pd^{II}, with oxidative addition of Pd^0 to the isomeric bromoimines **16** and **17**, a series of *N*-6-bromobenzyl-6′-bromobenzalimines (**21**) were prepared and treated with $Pd(dba)_2$ (Scheme 3). A series of dimeric-bridged dibromocyclopalladated benzalimines (**22a–22c**) was obtained, and these compounds were easily converted into the monomeric triphenylphosphine complexes **23a–23c**. In the ^1H NMR spectra of the latter, the imine proton absorbs at ca. 7.9δ and the CH_2 group at ca. 5.4δ. Additionally, in the complex **23b** one of the methoxy groups is shifted upfield by 2.83 ppm. In the ^{13}C NMR spectra of **23a–23c**, the Pd–C, N=C and CH_2 resonances occur at about 159, 175 and 62 ppm, respectively. These spectral data are very similar to those observed with **13a** and **13b** in which it has now been established that the C=N group is part of the pallodocyclic ring.

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