# Metal-Proton Interactions in Benzylamine Complexes of Palladium(II): The Effect of Methyl Substitution at Nitrogen and the Role of the Interaction During Cyclopalladation. X-Ray Crystal Structure of Tetrabenzylaminepalladium(II) Acetate Chloride

## Tony C. Jones,<sup>A</sup> Alastair J. Nielson<sup>A,B</sup> and Clifton E. Rickard<sup>A,C</sup>

<sup>A</sup> Department of Chemistry, University of Auckland,

Private Bag, Auckland, New Zealand.

<sup>B</sup> Author to whom correspondence should be addressed.

<sup>c</sup> Crystallography author.

#### Abstract

Reaction of  $Pd(O_2CMe)_2$  with  $PhCH_2NH_2$  leads to either  $Pd(NH_2CH_2Ph)_2(O_2CMe)_2$  or  $[Pd(NH_2CH_2Ph)_4][O_2CMe]_2$ . The X-ray crystal structure of  $[Pd(NH_2CH_2Ph)_4][Cl][O_2CMe]$  shows pairs of  $[Pd(NH_2CH_2Ph)_4]^{2+}$  ions held together by hydrogen bonds from the NH proton to chlorine and oxygen atoms of the anions, and the absence of interactions between phenyl ring *ortho* protons and the metal. PhCH\_2NHMe reacts with  $Pd(O_2CMe)_2$  giving  $Pd(NHMeCH_2Ph)_2(O_2CMe)$  and PhCH\_2NMe\_2 gives the cyclometallate  $[Pd(NMe_2CH_2Ph-C,N)(\mu-O_2CMe)]_2$ . <sup>1</sup>H n.m.r. spectra indicate that the complexes  $Pd(NMe_2CH_2Ph)(L)(O_2CMe)_2$  (L =  $PhNH_2$ ,  $o-MeC_6H_4NH_2$ ) prepared from  $[Pd(L)(O_2CMe)(\mu-O_2CMe)]_2$ , contain an interaction of the benzylamine *ortho* aromatic protons with the metal whereas  $Pd(NHMeCH_2Ph)(L)(O_2CMe)_2$  (L =  $o-MeC_6H_4NH_2$ ) does not. <sup>1</sup>H n.m.r. analysis of  $PdCl_4^{2-}$  and  $PhCH_2NMe_2$  in  $(^2H_1)$ methanol at 400 MHz indicates a 1 : 1 reaction stoichiometry and metal-proton interactions in intermediates containing above-plane and in-plane geometry of the aromatic ring, before metallation takes place. A 400-MHz spectral analysis of  $Pd(O_2CMe)_2$  and  $PhCH_2NMe_2$  in  $CDCl_3$  suggests similarly orientated species arise in the reaction giving  $[Pd(NMe_2CH_2Ph-C,N)(\mu-O_2CMe)]_2$ .

#### Introduction

Cyclopalladated benzylamine complexes are now convenient intermediates for several organic syntheses,<sup>1</sup> yet few aspects of the cyclometallation process are clearly understood. Early preparative studies<sup>2</sup> showed that palladium-carbon bonds were formed only with N,N-disubstituted benzylamines, indicating a steric requirement at nitrogen. Subsequently these ligands were found to cyclometallate on reaction with a variety of transition metals.<sup>3</sup> Complexes in which a ligand proton makes a close approach to the metal centre<sup>4-6</sup> have been suggested as intermediates during such

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<sup>&</sup>lt;sup>1</sup> See for example Thompson, J. M., and Heck, R. F., *J. Organomet. Chem.*, 1975, **40**, 2667; Holton, R. A., *Tetrahedron Lett.*, 1977, 355; Brisdon, B. J., Nair, P., and Dyke, S. F., *Tetrahedron*, 1981, **37**, 173; Grigor, B. A., and Nielson, A. J., *J. Organomet. Chem.*, 1977, **132**, 439.

<sup>&</sup>lt;sup>2</sup> Cope, A. C., and Friedrich, E. C., J. Am. Chem. Soc., 1968, 90, 909.

<sup>&</sup>lt;sup>3</sup> Omae, I., Chem. Rev., 1979, 79, 287.

<sup>&</sup>lt;sup>4</sup> Van Baar, J. F., Vrieze, K., and Stufkens, D. J., J. Organomet. Chem., 1974, 81, 247.

<sup>&</sup>lt;sup>5</sup> De Stefano, N. J., Johnson, D. K., and Venanzi, L. M., Helv. Chim. Acta, 1976, 59, 2683.

<sup>&</sup>lt;sup>6</sup> Nielson, A. J., Transition Met. Chem., 1981, 6, 180.

reactions<sup>4</sup> and were recently shown to occur during the cyclopalladation of 1-tetralone oximes.<sup>7</sup>

In the present work a study was carried out to correlate the degree of substitution at the benzylamine nitrogen, with formation of metal-proton interactions, and to establish the reaction pathways for any resulting cyclopalladations.

## **Results and Discussion**

## Preparation of Complexes

When benzylamine or *N*-methylbenzylamine are made to react with  $PdCl_4^{2-}$  in MeOH, the products are insoluble  $PdCl_2L_2$  complexes while *N*,*N*-dimethylbenzylamine cyclometallates.<sup>1</sup> To confer greater solubility, the ligands were treated with  $Pd(O_2CMe)_2$ .

Attempts to prepare complexes of the form  $[Pd(L)(O_2CMe)(\mu-O_2CMe)]_2$  which are stable for  $L = PhNH_2$  and similar aromatic amines<sup>6</sup> were not successful for benzylamine or *N*-methylbenzylamine. While reaction of  $Pd(O_2CMe)_2$  (trimeric



7 Nielson, A. J., J. Chem. Soc., Dalton Trans., 1981, 205.

in CHCl<sub>3</sub><sup>8</sup>) with one equivalent of PhCH<sub>2</sub>NH<sub>2</sub> gave a solid analysing as Pd(NH<sub>2</sub>CH<sub>2</sub>Ph)(O<sub>2</sub>CMe)<sub>2</sub>, <sup>1</sup>H n.m.r. spectra indicated that both Pd(O<sub>2</sub>CMe)<sub>2</sub> and the complex Pd(NH<sub>2</sub>CH<sub>2</sub>Ph)<sub>2</sub>(O<sub>2</sub>CMe)<sub>2</sub> (1) were present. This bis-complex was best prepared by using two equivalents of amine. Addition of excess benzylamine to Pd(O<sub>2</sub>CMe)<sub>2</sub> or complex (1) resulted in a colourless complex analysing as Pd(NH<sub>2</sub>CH<sub>2</sub>Ph)<sub>4</sub>(O<sub>2</sub>CMe)<sub>2</sub> which conductance measurements showed as a non-electrolyte, discounting the ionic species [Pd(NH<sub>2</sub>CH<sub>2</sub>Ph)<sub>4</sub>] [O<sub>2</sub>CMe]<sub>2</sub> (2). (However, see later.) Reaction of Pd(O<sub>2</sub>CMe)<sub>2</sub> with one or two equivalents of *N*-methylbenzylamine, or excess, gave Pd(NHMeCH<sub>2</sub>Ph)<sub>2</sub>(O<sub>2</sub>CMe)<sub>2</sub> (3) while *N*,*N*-dimethylbenzylamine cyclometallated giving [Pd(NMe<sub>2</sub>CH<sub>2</sub>Ph-C,*N*)( $\mu$ -O<sub>2</sub>CMe)]<sub>2</sub> (4) and producing MeCO<sub>2</sub>H.



Fig. 1. Molecular structure of  $[Pd(NH_2CH_2Ph)_4]$ -[Cl]  $[O_2CMe]$ . Atoms not otherwise designated are carbons.

Reactions were also studied that might lead to bis-amine complexes containing two different amines. Addition of one equivalent of benzylamine and *N*-methylbenzylamine together, to  $Pd(O_2CMe)_2$ , gave mixtures of complexes as shown by <sup>1</sup>H n.m.r. spectroscopy. Attempts to bridge-split the dimer  $[Pd(NH_2-o-MeC_6H_4)-(O_2CMe_3)(\mu-O_2CMe)]_2^{-6}$  with benzylamine also gave mixtures but *N*-methylbenzylamine gave the bis-amine complex Pd(NHMeCH<sub>2</sub>Ph)(NH<sub>2</sub>-o-MeC<sub>6</sub>H<sub>4</sub>)(O<sub>2</sub>CMe)<sub>2</sub> (5). However, the stability of this complex in solution was not great as <sup>1</sup>H n.m.r. spectra indicated that on standing for several hours mixtures of complexes were formed. On removal of solvent and re-extracting the residue, Pd(NHMeCH<sub>2</sub>Ph)<sub>2</sub>(O<sub>2</sub>CMe)<sub>2</sub> (3) was obtained, leaving a solid analysing closely as Pd(NH<sub>2</sub>-o-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>(O<sub>2</sub>CMe)<sub>2</sub>.

<sup>8</sup> Stephenson, T. A., Morehouse, S. M., Powell, A. R., Heffer, J. P., and Wilkinson, G., J. Chem. Soc., 1965, 3632.

Reaction of N,N-dimethylbenzylamine with the acetate-bridged dimers  $[Pd(L)-(O_2CMe)(\mu-OCMe)]_2$  (L = PhNH<sub>2</sub> or *o*-MeC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub><sup>6</sup>) gave the yellow bridge-split species Pd(NMe<sub>2</sub>CH<sub>2</sub>Ph)(L)(O<sub>2</sub>CMe)<sub>2</sub> [(6) and (7)] which on refluxing in CH<sub>2</sub>Cl<sub>2</sub> converted into the dimeric cyclopalladated complex di- $\mu$ -acetato-bis(N,N-dimethylbenzylamine-C,N)dipalladium (4).

Atom	x	у	Z	Atom	x	У	Z
Pd	0.1187(1)	0.1536(1)	0.48886(9)	C(16)	-0.096(2)	0.115(2)	0.121(1)
Cl	0.3116(4)	-0.1131(4)	0.5224(3)	C(21)	0.341(2)	0.236(1)	0.334(1)
<b>O</b> (1)	0.0710(1)	0.1700(1)	0.7452(7)	C(22)	0.348(2)	0.350(2)	0.390(1)
O(2)	-0.0940(1)	0.0830(1)	0.8049(7)	C(23)	0.327(2)	0.454(2)	0.353(1)
N(1)	-0.031(1)	0.108(1)	0.3725(7)	C(24)	0.303(2)	0.410(2)	0.249(1)
N(2)	0.236(1)	0.066(1)	0.3956(8)	C(25)	0.295(2)	0.295(2)	0.189(1)
N(3)	0.257(1)	0.177(1)	0.6099(8)	C(26)	0.316(2)	0.194(2)	0.232(1)
N(4)	-0.009(1)	0.229(1)	0.5781(9)	C(31)	0.458(1)	0.291(1)	0.739(1)
C(1)	-0.028(1)	0.182(1)	0.303(1)	C(32)	0.433(2)	0.336(2)	0.830(1)
C(2)	0.364(2)	0.133(2)	0.378(1)	C(33)	0.520(2)	0.338(2)	0.916(2)
C(3)	0.365(2)	0.291(1)	0.653(1)	C(34)	0.619(2)	0.281(2)	0.891(1)
C(4)	-0.028(2)	0.360(2)	0.593(1)	C(35)	0.654(2)	0.235(2)	0.806(2)
C(5)	0.013(2)	0.165(1)	0.816(1)	C(36)	0.565(2)	0.237(2)	0.720(1)
C(6)	0.072(2)	0.249(2)	0.918(1)	C(41)	0.088(2)	0.461(2)	0.653(1)
<b>C</b> (11)	-0.127(1)	0.119(1)	0.211(1)	C(42)	0.183(2)	0.515(2)	0.602(2)
C(12)	-0.260(2)	0.065(1)	0.214(1)	C(43)	0.289(2)	0.600(2)	0.657(2)
C(13)	-0.353(2)	0.007(2)	0.128(1)	C(44)	0.313(2)	0.638(2)	0.744(2)
C(14)	-0.314(2)	0.008(2)	0.038(1)	C(45)	0.232(2)	0.603(2)	0.807(2)
C(15)	-0.186(2)	0.060(2)	0.033(1)	C(46)	0.116(2)	0.505(2)	0.749(1)

Table 1. Fractional atomic coordinates for [Pd(NH<sub>2</sub>CH<sub>2</sub>Ph)<sub>4</sub>] [Cl] [OAc]

To confirm the presence of the  $[Pd(NH_2CH_2Ph)_4]^{2+}$  ion in (2) and to establish if any ortho aromatic ring hydrogens made a close approach to the metal centre, an X-ray structural determination was carried out. After recrystallization of (2) from  $CH_2Cl_2$ /hexane the crystal chosen was found to be  $[Pd(NH_2CH_2Ph)_4]$  [Cl]  $[O_2CMe_3]$ . Fig. 1 shows the structure of the complex which consists of a palladium atom coordinated by the nitrogens of four benzylamine ligands. Atomic coordinates are given in Table 1 and bond distances and angles in Table 2. The coordination geometry about palladium varies only slightly from square-planar and the Pd–N bond distances are in good agreement with those of other palladium amine complexes.<sup>9</sup> The shortest distances between palladium and chlorine or acetate oxygen are 4.0 and 3.71 Å, respectively, demonstrating the presence of discrete cations and anions.

The main feature of the structure is the hydrogen bonding of the N-H protons with the chloride ion and acetate oxygens which link the cations into pairs. Cl···H contacts range from  $2 \cdot 28(1)$  to  $2 \cdot 39(1)$  Å which are similar to those found in  $[Pd(en)_2] [Cl]_2$ .<sup>10</sup> Short O···H contacts are made between O(1) and H(2)N(4) as well as H(1)N(3) (1.86(2) and 1.90(2) Å respectively, Pd-O(1) distance  $3 \cdot 71(1)$  Å) and between H'(2)N'(2) and O(2) (1.95(2) Å, Pd'-O(2) distance  $4 \cdot 14$  Å). The remaining hydrogen H(1)N(2) is separated from O(2) by  $2 \cdot 53(2)$  Å. Layers of cations

<sup>&</sup>lt;sup>9</sup> Hartley, F. R., 'The Chemistry of Platinum and Palladium' p. 470 (Applied Science Publishers Ltd: London 1973).

<sup>&</sup>lt;sup>10</sup> Wiesner, J. R., and Lingafelter, E. C, Inorg. Chem., 1966, 5, 1770.

and their associated anions are not held together by interlayer hydrogen bonding as found for  $[Pd(en)_2] [Cl]_2^{10}$  or  $[Pt(NH_3)_2(NHMe_2)_2] [Cl]_2^{11}$  these distances in the complex being greater than  $4 \cdot 0$  Å.

Atoms	Value	Atoms	Value
	Bond le	ngths (Å)	
N(1)-Pd	2.033(7)	N(2)-Pd	2.007(10)
N(3)-Pd	2.066(7)	N(4)-Pd	2.004(10)
C(1) - N(1)	1.518(11)	C(2)-N(2)	1 · 486(13)
C(3) - N(3)	1.466(12)	C(4)-N(4)	1.492(13)
C(11)-C(1)	$1 \cdot 473(12)$	C(21)-C(2)	1 · 553(14)
C(31)-C(3)	1 · 500(13)	C(41)–C(4)	1.470(14)
	Bond angl	es (degrees)	
N(1)-Pd-N(2)	90.3(3)	N(1)-Pd-N(3)	171.9(3)
N(1)-Pd-N(4)	87.3(3)	N(2)-Pd-N(3)	<b>90</b> ·3(3)
N(2)-Pd-N(4)	$175 \cdot 7(4)$	N(3)-Pd-N(4)	91·5(3)
Pd-N(1)-C(1)	121.3(6)	Pd-N(2)-C(2) ·	$124 \cdot 0(7)$
Pd-N(3)-C(3)	121.5(6)	Pd-N(4)-C(4)	120.6(7)
N(1)-C(1)-C(11)	113.5(8)	N(2)-C(2)-C(21)	110 · <b>9</b> (8)
N(3)-C(3)-C(31)	114.3(9)	N(4)-C(4)-C(41)	113·9(9)
O(1)-C(5)-O(2)	$122 \cdot 3(12)$	O(1)-C(5)-C(6)	120.5(12)
O(2)-C(5)-C(6)	117.0(12)		

Table 2. Selected bond lengths and angles for [Pd(NH<sub>2</sub>CH<sub>2</sub>Ph)<sub>4</sub>] [Cl] [OAc]

Pairing of the cations by hydrogen bonding causes the slight distortion away from square-planar geometry while the phenyl rings of the ligands are forced to adopt orientations above or below the cationic pair. The closest approach of *ortho* aromatic hydrogens to the metal at  $3 \cdot 35$  and  $3 \cdot 56$  Å, made by those protons at C(22) and C(42) of the two phenyl groups orientated over the top of the square plane, clearly show the absence of metal-proton interactions which is also indicated by the <sup>1</sup>H n.m.r. spectrum of (2) (see later).

The low conductance figures obtained for (2) remain unexplained. However, it is possible that some residual hydrogen bonding may remain on dissolving the solid, if  $N-H\cdots O$  bridging occurs across pairs of palladium cations bound by four acetate groups.

## N.M.R. Spectra

The free ligands show broad resonances for the NH protons, where applicable, as a result of inversion and proton exchange processes.<sup>12</sup> Coordination of nitrogen inhibits inversion so that in the complexes proton exchange should be the only observable kinetic process leading to peak broadening. For  $Pd(NH_2CH_2Ph)_2$ - $(O_2CMe)_2$  (1) both the benzylic methylene and NH proton resonances were broadened and lacked fine structure. The benzylic resonances collapsed slowly to a broadened singlet on addition of  $D_2O$ , indicating proton exchange for the coordinated primary

<sup>&</sup>lt;sup>11</sup> Anderson, J. S., Carmichael, J. W., and Cordes, A. W., Inorg. Chem., 1970, 9, 143.

<sup>&</sup>lt;sup>12</sup> Jackman, L. M., and Sternhell, S., 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry' p. 366 (Pergamon Press: Oxford 1969).

amine. While the NH proton resonance for  $Pd(NHMeCH_2Ph)_2(O_2CMe)_2$  appeared as a broad resonance, the benzylic methylene group showed the features of an AB quartet (asymmetry provided at nitrogen) additionally coupled to the NH proton  $(J_{AB} 14 \text{ Hz}, J_{NH,CH} 8 \text{ Hz})$ , and the N-methyl resonance a well defined doublet  $(J_{CH,NH} 8 \text{ Hz})$ , which suggested slow proton exchange. No change in the spectrum was recorded after  $D_2O$  contact with the complex in solution for several days; this indicated negligible proton exchange. The spectrum of the complex prepared from MeNDCH<sub>2</sub>Ph showed a slightly broadened methylene-proton AB quartet  $(J_{AB} 18 \text{ Hz})$  and methyl group singlet. Contact of the solution with H<sub>2</sub>O over several days caused no spectral change. Thus, in separating out kinetic processes the main contributor to NH proton broadening for the coordinated ligand most likely arises from nitrogen nuclear quadrupole effects. The results also suggest that, if ligand interchange does occur in solution, inter- or intra-molecular processes operate without dissociation to the free ligand. The stability of the bis-amine complex is also shown by the inability to form a dimeric acetate-bridged complex and also by the lability of mixed ligand complexes.

The ionic species  $[Pd(NH_2CH_2Ph)_4][O_2CMe]_2$  also showed broad resonances for the benzylic methylene and NH protons. Addition of  $D_2O$  gave a broad singlet for the methylene protons and a broadened one-proton triplet in the amine proton region, which decreased in intensity on standing. The NH triplet most likely arises from a CH<sub>2</sub>-NHD moiety and suggests rapid deuterium exchange of one NH proton and less rapid for the second.

Complex	Free ligand <sup>A</sup>	Complex <sup>A</sup>	$\Delta \delta^{\mathrm{B}}$
$Pd(NH_2CH_2Ph)_2(O_2CMe)_2 (1)$	7.25	7.32	0.07
$[Pd(NH_2CH_2Ph)_4][O_2CMe]_2$ (2)	7.25	7.33	0.08
$Pd(NHMeCH_2Ph)_2(O_2CMe)_2$ (3)	7.32	7.36	0.04
$Pd(NHMeCH_2Ph)(NH_2-o-MeC_6H_4)(O_2CMe)_2$ (5)	7.32	7.43	0.11
	(2·09) <sup>c</sup>	(2·44) <sup>c</sup>	(0·35) <sup>c</sup>
$Pd(NMe_2CH_2Ph)(NH_2Ph)(O_2CMe)_2$ (6)	7.20	$7 \cdot 25 m, p$	0.05 m, p
		7.92 0	0·72 o
$Pd(NMe_2CH_2Ph)(NH_2-\rho-MeC_6H_4)(O_2CMe)_2$ (7)	7.20	$7 \cdot 36 m, p$	0.16 m, p
		7.90 o	0·70 o
		(2·48) <sup>c</sup>	(0·39) <sup>c</sup>

Table 3.	Aromatic proton reso	nance shifts ( $\Delta\delta$ ) f	for coordinated ben	zylamines
١	alues given for CDCl	3 solution, concen	tration independen	t

<sup>A</sup> o, m, p Protons, centre of singlet or multiplet, ppm from SiMe<sub>4</sub>. <sup>B</sup>  $\Delta \delta = \delta$ (complex) –  $\delta$ (free ligand). <sup>c</sup> Values in parentheses for the methyl resonance of o-toluidine.

In general small downfield shifts of the ligand aromatic protons occurred on coordination (see Table 3). Downfield shifts of the *ortho* aromatic protons characteristic of metal-proton interactions,<sup>4-6</sup> were not observed for coordinated benzylamine or *N*-methylbenzylamine and cyclometallation did not occur on standing or refluxing the solutions. However, for the complexes  $Pd(NMe_2CH_2Ph)(L)(O_2CMe)_2$ , (L = PhNH<sub>2</sub>, *o*-MeC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>), the *ortho* aromatic protons of *N*,*N*-dimethylbenzylamine showed a downfield shift of 0.72 and 0.70 ppm compared with the free ligand. Both *ortho* protons were contained in the observed multiplet; this indicated rapid Ph-CH<sub>2</sub> bond rotation on the n.m.r. time scale. Molecular models show inhibition

of N-CH<sub>2</sub> bond rotation by steric interaction of *ortho* aromatic protons with N-methyl groups and inhibited N-Pd bond rotation by restriction of aromatic ring movement by the *trans* acetate groups [see structures (6) and (7)].

The downfield shift thus represents time averaging of the *ortho* protons in and out of the  $d_{z^2}$  anisotropic cone during predominant Ph-CH<sub>2</sub> bond rotation.

The complex  $Pd(NMe_2CH_2Ph)(NH_2-o-MeC_6H_4)(O_2CMe)_2$  (7) contains an additional interaction between the metal centre and ortho-methyl substituent of coordinated o-toluidine, the downfield shift (0.39 ppm) similar in magnitude to that found for the monomeric complexes  $Pd(O_2CMe)_2L_2$  and  $RhCl(CO)_2(L)$  (L =  $o-MeC_6H_4NH_2$ ).<sup>6</sup> Ph–CH<sub>3</sub> and PhN– bond rotations are unrestricted [see structure (7)] so that the shift is an average for the three protons as well as Ph-N bond rotation taking the ortho-methyl substituent away from the anisotropy cone. Downfield shifts of the N,N-dimethylbenzylamine ortho protons are similar in Pd(NMe<sub>2</sub>CH<sub>2</sub>Ph)- $(NH_2-o-MeC_6H_4)(O_2CMe)_2$  (7) and  $Pd(NMe_2CH_2Ph)(NH_2Ph)(O_2CMe)_2$ (6) showing that an additional metal-proton interaction in the sixth coordination site has little effect. Similarly the shift downfield of the o-toluidine methyl resonance in  $Pd(NMe_2CH_2Ph)(NH_2-o-MeC_6H_4)(O_2CMe)_2$  (7) and  $Pd(NHMeCH_2Ph)(NH_2-MeC_6H_4)(O_2CMe)_2$  (7) and  $Pd(NHMeCH_2Ph)(O_2CMe)_2$  (7) and  $Pd(NHMeCH_2Ph)(NH_2Ph)(O_2CMe)_2$  (7) and  $Pd(NHMeCH_2Ph)(NH_2$  $o-MeC_6H_4)(O_2CMe)_2$  (5) shows little variation. In the latter complex a downfield shift of the N-methylbenzylamine ortho aromatics does not occur. While molecular models indicate that the PhCH<sub>2</sub>NH<sub>2</sub> and PhCH<sub>2</sub>NHMe ligands could coordinate with the aromatic ring above the coordination plane, such a geometry is clearly repulsive in nature and only occurs when N,N-dimethyl groups force the aromatic ring to adopt an above-plane configuration. The metal-proton interactions contained in these complexes are likely to be similar in magnitude to the weak interaction  $(M \cdots H \text{ distance } 2 \cdot 3 - 2 \cdot 8 \text{ Å})$  shown by X-ray crystallography to occur in complexes with comparable ortho aromatic proton downfield shifts.<sup>13-15</sup>

### **Mechanistic Studies**

<sup>1</sup>H n.m.r. spectral analysis of *N*,*N*-dimethylbenzylamine and  $PdCl_4^{2-}$  (2:1) in  $CD_3OD$  showed only one equivalent of ligand coordinated with the second remaining free throughout a series of spectral events. At 90 MHz a 1:1 mixture of ligand and  $PdCl_4^{2-}$  exhibited three components: species A recorded a downfield shift ( $\Delta$ ) of 1.05 ppm for the *ortho* aromatic protons ( $A_{ortho}$ ) compared with the free ligand, characteristic of above plane geometry; species B with the *ortho* proton resonance ( $B_{ortho}$ ) shifted upfield, suggestive of in-plane geometry,<sup>7</sup> and species C, integrated correctly for a soluble cyclometallated product. A spectrum obtained at  $-70^{\circ}C$  after mixing the components at dry ice temperature showed the presence of A only, while B did not appear until 10°C.

A well resolved spectrum obtained at 400 MHz (Fig. 2) showed  $A_{ortho}$  to consist of A'<sub>ortho</sub> (80%,  $\Delta 1.05$  ppm) and A"<sub>ortho</sub> (20%,  $\Delta 0.90$ ) and for  $B_{ortho} \Delta$  was 0.40 ppm. With loss of above plane geometry in B the anisotropy experienced by  $B_{ortho}$ , while involving Ph-CH<sub>2</sub> bond rotation time averaging effects, as for  $A_{ortho}$ , could in addition involve effects arising from Pd-N bond rotation leading to above- or below-plane

<sup>&</sup>lt;sup>13</sup> Roe, D. M., Bailey, P. M., Moseley, K., and Maitlis, P. M., J. Chem. Soc., Chem. Commun., 1972, 1273.

<sup>&</sup>lt;sup>14</sup> Constable, A. G., McDonald, W. S., and Shaw, B. L., J. Chem. Soc., Dalton Trans., 1979, 1109.

<sup>&</sup>lt;sup>15</sup> Otsuka, S., Yoshida, T., Matsumoto, M., and Nakatsu, K., J. Am. Chem. Soc., 1976, 98, 5850.

rotamers, so that purely in-plane geometry may not exist. However, no evidence for this was obtained down to  $-70^{\circ}$ C as found for other complexes of *N*,*N*-dimethylbenzylamine.<sup>16</sup> At low temperature B did not convert back into A. Formation of A could easily result from reaction of the amine with Li<sub>2</sub> [PdCl<sub>4</sub>] or Li<sub>2</sub> [PdCl<sub>6</sub>] thought to be present in solutions of Li<sub>2</sub> [PdCl<sub>4</sub>].<sup>17</sup> As the spectral features are similar to those observed for the cyclopalladation of 1-tetralone oxime<sup>7</sup> a similar mechanism should operate (Scheme 1).



<sup>16</sup> Deeming, A. J., and Rothwell, I. P., J. Chem. Soc., Dalton Trans., 1978, 1497.
<sup>17</sup> Baar, N., and Dyke, S. F., J. Organomet. Chem., 1983, 243, 223.

Analysis of the change in percentage composition with time (Fig. 3a) showed B increased at the expense of A until the point of rapid precipitation (20 min) of the cyclopalladated complex, when B declined rapidly.



Fig. 3. Change in (a) composition (b) NMe<sub>2</sub> group peak area with time for A, B and C in the 400 MHz <sup>1</sup>H n.m.r. spectra of N, N-dimethylbenzylamine/PdCl<sub>4</sub><sup>2-</sup> (1:1) in CD<sub>3</sub>OD. First spectrum obtained 30 s from mixing. Rapid precipitation of cyclopalladation product after 20 min from mixing.

From the relative peak area (Fig. 3b) it is seen that the decline of A was more rapid than the build-up of B or C, with the concentration of C reaching a maximum much earlier than B. While B formed at the expense of A, the rate was not equal, although B rose to form the major component (60%). Initial increase in B was offset by increase in C, the latter component reaching a maximum of 15% total composition before decreasing to an approximately 10% composition after 10 min. The slow step in the reaction is thus conversion of B into C, although it is apparent that conversion of C into the precipitated dimer affects the conversion of B into C. The spectra do not show resonances characteristic of Whelund intermediates or  $\sigma$ -complexes so that a concerted process for the transformation of B into C is likely.<sup>7</sup>

Analysis of the Pd(OAc)<sub>2</sub>/N,N-dimethylbenzylamine reaction at 90 MHz showed a 1:1 reaction stoichiometry, with an initial downfield shift of the *ortho* aromatic protons but spectral resolution of the ensuing events was poor. At 400 MHz, a spectrum obtained 30 s from mixing the reactants indicated the presence of three different species, each showing a downfield shift of the *ortho* aromatic protons: D, 7%,  $\Delta$  0.96; E, 60%,  $\Delta$  0.62 and F, 33%,  $\Delta$  0.54 ppm (see Fig. 4b). The benzylic methylene protons exhibited a singlet for D and F and an AB quartet for E, while the NMe<sub>2</sub> groups of D and F appeared as a singlet and as a doublet for E. The observance of acetate methyl resonances for E characteristic of bridging and terminal acetate ligands [ $\delta 2.00$ , and 1.75 ppm {cf. 1.76 ppm in Pd(NMe<sub>2</sub>CH<sub>2</sub>Ph)(NH<sub>2</sub>o-MeC<sub>6</sub>H<sub>4</sub>)(O<sub>2</sub>CMe)<sub>2</sub> (7)}] suggest structure (8) where the [Pd-acetate]<sub>2</sub> bridging system adopts a boat configuration,<sup>17-20</sup> although a distorted chair form is also possible. The two-proton doublet for the *ortho* aromatics indicates rapid bond rotation about the Ph-CH<sub>2</sub> bond. While asymmetric structure (8) would give rise to the methylene AB quartet, the singlets for D(CH<sub>2</sub>) and F(CH<sub>2</sub>) suggest symmetrical structures which are not readily apparent with the acetate methyl resonances appearing to be those of bridging acetates.\*



\* Two singlets are expected for the NMe<sub>2</sub> protons and an AB quartet for the CH<sub>2</sub> protons if the coordination plane of palladium is not a plane of symmetry, whereas two singlets should arise if a plane of symmetry exists. The two singlets observed for  $Pd(NMe_2CH_2Ph)(NH_2-o-MeC_6H_4)-(O_2CMe)_2$  (7) suggests that methylene protons will be sensitive to asymmetry provided only by the acetate ligands.

<sup>18</sup> Wong-Ng, W., Cheng, P. T., Kocman, V., Lüth, H., and Nyburg, S. C., *Inorg. Chem.*, 1979, **18**, 2620.

<sup>19</sup> Churchill, M. R., Wasserman, H. J., and Young, G. J., Inorg. Chem., 1980, 19, 762.

<sup>20</sup> Powell, J., and Jack, T., Inorg. Chem., 1972, 11, 1039.

Tetrabenzylaminepalladium(II) Acetate Chloride

Spectra obtained at 30-s intervals indicated E increased at the expense of D and F; this was not reversed on lowering the temperature to  $-40^{\circ}$ C, but merely slowed down. At  $-40^{\circ}$ C the ligand reacted only slowly with Pd(OAc)<sub>2</sub> while F became the main component with time when the mixture was held at 0°C.

At ambient temperature, loss of spectral characteristics for E was offset by an increase in resonances attributable to a non-cyclometallate G and a cyclometallate H, the latter being different from the cyclometallated dimer I (see Fig. 4c-e). The upfield shift of the ortho aromatic protons in G compared with the remainder suggests that an in-plane metal-proton interaction exists or that time averaging of aboveand below-plane rotamers occurs. However, no spectral change was recorded down to  $-40^{\circ}$ C with the two proton *ortho* resonances showing Ph-CH<sub>2</sub> bond rotation was still rapid at this temperature.\* It is not possible to assign the individual methylene AB quartets unequivocally to either G or H but as the sum of G and H, and interestingly, the B (or A) parts of the two AB quartets are accidentally equivalent and remain so at  $-40^{\circ}$ C. Studies with Pd(O<sub>2</sub>CCD<sub>3</sub>)<sub>2</sub> indicate the NMe<sub>2</sub> resonances of G and H are similar to those of dimer I, which suggests the environment of the methyl groups is similar in G, H and I. Although conclusive evidence is not available, an unsymmetrical molecule with oxygens of bridging or nearly bridging ligands loosely coordinated to available fifth or fifth-and-sixth coordination sites may stabilize a purely in-plane interaction in G, and in the cyclometallate H, before the formation of dimer I. The ratio of G to H apparently remains constant, even at lower temperature, so that any intermediate formed between (e.g. Whelund intermediate or  $\sigma$  complex) has a very short life on the n.m.r. time scale. Further, the transformation of G to H may not be reversible as the reaction readily goes to completion in the presence of the MeCO<sub>2</sub>H produced. In this regard it is noted that cyclopalladation of aromatic imines occurs readily with Pd(O<sub>2</sub>CMe)<sub>2</sub> in MeCO<sub>2</sub>H.<sup>21</sup>

#### Experimental

Microanalytical data were obtained by Professor A. D. Campbell and associates, University of Otago, New Zealand. Melting points were determined on a Reichert-Kofler hotbench or Kofler hot stage apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 457 instrument as pressed KBr discs or as Nujol mulls between CsI plates. <sup>1</sup>H n.m.r. spectra were recorded at 60 and 90 MHz on Varian T-60 and Perkin-Elmer R32 spectrometers and at 400 MHz on a Bruker WH400 instrument at Queen Mary College, London.

#### Bisacetatobisbenzylaminepalladium(II) (1)

Benzylamine (0·1 g, 9·3 mmol) in  $CH_2Cl_2$  (10 cm<sup>3</sup>) was added to palladium acetate (0·1 g, 0·45 mmol) dissolved in  $CH_2Cl_2$  (20 cm<sup>3</sup>) and the mixture stirred for 10 minutes. The solution was filtered, the solvent removed in a vacuum, to give a white crystalline material. Recrystallization from  $CH_2Cl_2$ /light petroleum gave the *complex* as white crystals (0·13 g, 67%), m.p. 120–121° (Found: C, 49·0; H, 5·5; N, 6·2.  $C_{18}H_{24}N_2O_2Pd$  requires C, 49·3; H, 5·5; N, 6·4%).

I.r. (CsI) 3145 (NH); 1628 (NH); 1580 ( $\nu$ (OCO)<sub>asym</sub>, unidentate); 1490; 1450; 1400; 1328 ( $\nu$ (OCO)<sub>sym</sub>, unidentate); 1250; 1172; 1074; 995; 915; 752, 708, 641 (monosubstituted benzene); 585; 475 (monosubstituted benzene); 372; 355 cm<sup>-1</sup>.

\* Below  $-40^{\circ}$ C the solution becomes viscous and a gummy material often separates. Solubility problems have also been encountered with other solvents at low temperature so that convincing spectra relating to any inherent dynamic processes have remained elusive. Lower temperatures apparently slow the transformations observed at ambient temperature as similarly found for CD<sub>3</sub>OD solutions of PdCl<sub>4</sub><sup>2-</sup> and PhCH<sub>2</sub>NMe<sub>2</sub> or 1-tetralone oxime.<sup>7</sup>

<sup>21</sup> Onoue, H., and Moritani, I., J. Organomet. Chem., 1972, 43, 431.

<sup>1</sup>H n.m.r.  $\delta$  (CDCl<sub>3</sub>, 60 MHz) 1.84, s, 3H, Me; 3.70, m (D<sub>2</sub>O, s), 2H, benzylic CH<sub>2</sub>; 4.18, m (D<sub>2</sub>O exchange), 2H, NH<sub>2</sub>; 7.32, s, 5H, aromatic.

#### Tetrabenzylaminepalladium(II) Diacetate (2)

Excess benzylamine was added to palladium acetate (0.2 g, 0.8 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 cm<sup>3</sup>) and the solution stirred for several hours. The colourless solution was filtered, the solvent removed in a vacuum and the residue recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/light petroleum to give the *complex* as colourless crystals (0.52 g, 90%), m.p. 150° (Found: C, 58.5; H, 6.5; N, 8.6. C<sub>32</sub>H<sub>42</sub>N<sub>4</sub>O<sub>4</sub>Pd requires C, 58.8; H, 6.5; N, 8.6%).

I.r. (CsI, Nujol) 3100, 1625 (NH); 1535 ((OCO)<sub>asym</sub>); 1495; 1450; 1390 ((OCO)<sub>sym</sub>); 1330; 1250; 1175; 1078; 995; 916; 868; 782; 754, 695, 642 (monosubstituted benzene); 615; 485; 365, 310, 285 cm<sup>-1</sup>.

<sup>1</sup>H n.m.r.  $\delta$  (CDCl<sub>3</sub>, 60 MHz) 1·36, s, 6H, O<sub>2</sub>CMe; 2·54, b (D<sub>2</sub>O, s), 8H, benzylic CH<sub>2</sub>; 6·0, 8H (D<sub>2</sub>O exchange), NH<sub>2</sub>; 7·33, m, 20H, aromatic.  $\Lambda_m 8\cdot4$  S cm<sup>2</sup> mol<sup>-1</sup> (1·034×10<sup>-3</sup> mol l<sup>-1</sup>, in nitromethane).

#### Bisacetatobis(N-methylbenzylamine)palladium(II) (3)

*N*-Methylbenzylamine (0·12 g, 1·0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>) was added dropwise to a solution of palladium acetate (100 mg, 0·45 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (25 cm<sup>3</sup>) and the mixture stirred for 30 min. The solvent was removed in a vacuum and the residue dissolved in diethyl ether (30 cm<sup>3</sup>), the solution filtered and reduced to half volume. On standing at 0° the *complex* was obtained as yellow crystals (0·13 g, 64%), m.p. 122° (Found: C, 51·6; H, 6·1; N, 6·0. C<sub>20</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>Pd requires C, 51·5; H, 6·0; N, 6·0%).

I.r. (KBr) 3180 (NH); 3044, 3030, 3005, 2980 (aromatic C–H); 2920, 2865 (aliphatic C–H); 1610 (NH); 1585 ( $\nu$ (OCO)<sub>sym</sub>, unidentate); 1495; 1460; 1410; 1375; 1360; 1320 ( $\nu$ (OCO)<sub>sym</sub>, unidentate); 1215; 1174; 1062; 1050; 1035; 1015; 945; 912; 750, 698, 615 (monosubstituted benzene); 530; 511; 482 (monosubstituted benzene); 332; 318; 265 cm<sup>-1</sup>.

<sup>1</sup>H n.m.r. (CDCl<sub>3</sub>, 90 MHz) 1·80, s, 6H, *trans* O<sub>2</sub>CMe; 2·22, d, J 8 Hz, 6H, NMe; 3·17 and 4·0, octet,  $J_{AB}$  14Hz,  $J_{CH,NH}$  8 Hz, 4H, benzylic CH<sub>2</sub>; 7·36, m, 10H, aromatic.

#### Bisacetatobis [(N-D)-N-methylbenzylamine] palladium(II) (D)-(3)

*N*-Methylbenzylamine in CH<sub>2</sub>Cl<sub>2</sub> was shaken with D<sub>2</sub>O and the organic layer separated and dried over MgSO<sub>4</sub>. The solvent was removed in a vacuum and the process repeated twice more. <sup>1</sup>H n.m.r. ( $\delta$  60 MHz) 2·40, s, 3H, NMe; 3·70, s, 2H, benzylic-CH<sub>2</sub>; 7·23, s, 5H, aromatic.

The complex was prepared as for the N-benzylamine ligand above.

<sup>1</sup>H n.m.r. ( $\delta$ , 60 MHz) 1.83, s, 6H, O<sub>2</sub>CMe; 2.13, s, 6H, NMe; 3.15 and 3.92, q, J 18 Hz, 4H, benzylic-CH<sub>2</sub>; 7.48, m, 10H, aromatic.

#### $Di-\mu$ -acetato-bis (N,N-dimethylbenzylamine-C,N)dipalladium(II) (4)<sup>22</sup>

*N*,*N*-Dimethylbenzylamine (0·18 g, 1·3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>) was added to palladium acetate (0·3 g, 1·3 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>) and the solution stirred for 2 h. The solution was filtered, light petroleum was added until cloudy and on standing the *complex* was obtained as yellow crystals (0·18 g, 75%). M.p. dec. >110° (Found: C, 44·7; H, 5·0; N, 4·7. C<sub>22</sub>H<sub>30</sub>N<sub>2</sub>O<sub>4</sub>Pd<sub>2</sub> requires C, 44·1; H, 5·0; N, 4·7%).

I.r. (KBr) 3040 (aromatic C-H); 2990, 2908, 2880, 2850 (C-H); 1580; 1560 ( $\nu$ (OCO)<sub>asym</sub>, bridge); 1445; 1432; 1410 ( $\nu$ (OCO)<sub>sym</sub>, bridge); 1342; 1235; 1015; 986; 967; 869; 848; 740, 681 (*ortho* disubstituted benzene); 620; 520; 554; 430; 332 cm<sup>-1</sup>.

<sup>1</sup>H n.m.r.  $\delta$  (CDCl<sub>3</sub>, 60 MHz) 2.05, s, 6H, NMe and  $\mu$ -O<sub>2</sub>CMe; 2.82, s, 3H, NMe; 3.09 and 3.64, q, J 14 Hz, 2H, benzylic CH<sub>2</sub>; 7.0, m, 4H, aromatic; (CDCl<sub>3</sub>, 400 MHz) 2.08 and 2.09, 2s, 6H, NMe and  $\mu$ -O<sub>2</sub>CMe; s, 3H, NMe; 3.08 and 3.55, q, J 14 Hz, 2H, benzylic CH<sub>2</sub>; 6.88, m, 2H, aromatic; 6.99, m, 2H, aromatic.

<sup>22</sup> Thompson, J. M., and Heck, R. F., J. Org. Chem., 1975, 40, 2667.

#### $Di-\mu-[(D_3)acetato]-bis$ (N,N-dimethylbenzylamine-C,N)dipalladium(II) ( $D_3$ )-(4)

Palladium acetate (0.15 g) was suspended in  $(D_4)$  acetic acid  $(0.5 \text{ cm}^3)$  and the mixture refluxed gently for 5 min after which the solution was cooled and the solvent removed in a vacuum. The process was repeated three times in all giving approximately 95% Pd $(O_2CD_3)_2$  by <sup>1</sup>H n.m.r. analysis (comparison with a known amount of SiMe<sub>4</sub>). N,N-Dimethylbenzylamine (0.06 g, 0.45 mmol)in CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>) was added to Pd $(O_2CD_3)_2$  (0.1 g, 0.45 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) and the solution stirred for 30 min. After filtering the solvent was removed in a vacuum leaving the complex as a yellow solid.

<sup>1</sup>H n.m.r.  $\delta$  (CDCl<sub>3</sub>, 60 MHz) 2 · 04, s, 3H, NMe; 2 · 82, s, 3H, NMe; 3 · 09 and 3 · 64, q, J 14 Hz, benzylic CH<sub>2</sub>; 7 · 0, m, 4H, aromatic.

#### Bisacetato-N-methylbenzylamine-0-toluidinepalladium(II) (5)

o-Toluidine (0.48 g, 0.45 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 cm<sup>3</sup>) was added to palladium acetate (0.1 g, 45 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) and the solution stirred for 5 min. N-Methylbenzylamine (54 mg, 0.45 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 cm<sup>3</sup>) was added dropwise, the solution stirred for a further 10 min and the solvent removed in a vacuum to give a yellow solid which was dissolved in ether, the volume reduced to c. 10 cm<sup>3</sup>. The solution was left to stand at  $-76^{\circ}$  for 15 min, giving the *complex* as a yellow microcrystalline solid (0.12 g, 57%), m.p. 108° (Found: C, 50.2; H, 5.8; N, 6.2. C<sub>19</sub>H<sub>25</sub>N<sub>2</sub>O<sub>4</sub>Pd requires C, 50.4; H, 5.8; N, 6.2%).

I.r. (KBr) 3220, 3188 (NH); 3050, 3038 (aromatic C–H); 2928, 2875 (NH and C–H); 1590 (broad, NH and  $\nu$ (OCO)<sub>asym</sub>, unidentate); 1500; 1460; 1410; 1375; 1322 or 1308 ( $\nu$ (OCO)<sub>sym</sub>, unidentate); 1130; 1065; 1052; 1038; 1028; 920; 750 (mono and 1,2-disubstituted benzene); 698 (monosubstituted benzene); 615; 525; 490; 440; 315 cm<sup>-1</sup>.

<sup>1</sup>H n.m.r.  $\delta$  (CDCl<sub>3</sub>, 60 MHz) 1 · 86, s, 6H, O<sub>2</sub>CMe; 2 · 00, d, J 8 Hz, 3H, NMe; 2 · 44, s, 3H, Me; 3 · 26 and 4 · 08, octet,  $J_{AB}$  15 Hz,  $J_{CH,NH}$  8 Hz, 2H, benzylic CH<sub>2</sub>; 6 · 32 and 6 · 6 broad, NH; 7 · 35, s, 4H, aromatic (*o*-toluidine); 7 · 43, m, 5H, aromatic (*N*-methylbenzylamine). On standing the solution the methyl-group resonances become more complex:  $\delta$  values at 1 · 71, 1 · 86, 2 · 00 (d, J 8 Hz), 2 · 19, 2 · 28, 2 · 35, 2 · 44, 2 · 59.

#### Bisacetatoanilino-N,N-dimethylbenzylaminepalladium(II) (6)

Aniline (41  $\cdot$  5 mg, 0  $\cdot$  45 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 cm<sup>3</sup>) was added dropwise to a rapidly stirred solution of palladium acetate (0  $\cdot$  1 g, 0  $\cdot$  45 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) and the orange-red solution stirred for 5 min. *N*,*N*-Dimethylbenzylamine (60 mg, 0  $\cdot$  45 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 cm<sup>3</sup>) was added and the stirring continued for 10 min. The solution was filtered and the solvent removed in a vacuum to give the *complex* as a yellow solid, m.p. dec. >95° (Found: C, 50  $\cdot$ 4; H, 6  $\cdot$ 0; N, 5  $\cdot$ 8. C<sub>19</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>Pd requires C, 50  $\cdot$ 4; H, 5  $\cdot$ 8; N, 6  $\cdot$ 1%).

I.r. (KBr) 3400, 3200 (NH); 3100, 3080, 3060 (aromatic C-H); 2960, 2918 (NH); 1630 (NH); 1582 ( $\nu$ (OCO)<sub>asym</sub>, unidentate); 1565; 1494; 1450; 1415; 1373; 1315 ( $\nu$ (OCO)<sub>sym</sub>, unidentate); 1235; 1015; 845; 765, 746, 705, 684 (monosubstituted benzene); 620; 531; 485; 430, 330 cm<sup>-1</sup>.

<sup>1</sup>H n.m.r.  $\delta$  (CDCl<sub>3</sub>, 60 MHz) 1.81, s, 6H, O<sub>2</sub>CMe; 2.28, s, 6H, NMe<sub>2</sub>; 3.52, s, 2H, benzylic CH<sub>2</sub>; 7.12, s, 4H, aromatic (aniline); 7.23 (obscured) b, 2H, NH<sub>2</sub>; 7.25, m, 3H, *m*- and *p*-aromatic (*N*,*N*-dimethylbenzylamine); 7.92, m, 2H, *o*-aromatic (*N*,*N*-dimethylbenzylamine).

The complex was refluxed for 30 min in  $CHCl_3$  (30 cm<sup>3</sup>) and the solvent removed. The residue was washed with light petroleum and recrystallized from  $CH_2Cl_2/light$  petroleum to give di- $\mu$ -acetato-bis(N,N-dimethylbenzylamine-C,N)dipalladium(II). Identical decomposition point, i.r. and <sup>1</sup>H n.m.r. spectrum to an authentic sample.

#### *Bisacetato*-N,N-*dimethylbenzylamine*-0-*toluidinepalladium*(II) (7)

o-Toluidine (48 mg, 0.45 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 cm<sup>3</sup>) was added dropwise to a solution of palladium acetate (0.1 g, 0.45 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) and the orange-red solution stirred for 5 min. N,N-Dimethylbenzylamine (60 mg, 0.45 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 cm<sup>3</sup>) was added slowly and the stirring continued for 10 min. The solvent was removed in a vacuum to give a gum which was stirred with light petroleum (5 cm<sup>3</sup>) and the solution filtered, the *complex* being left as a yellow solid (0.21 g,

100%), m.p. 109° (Found: C, 51.9; H, 6.0; N, 6.0.  $C_{20}H_{27}N_2O_4Pd$  requires C, 51.5; H, 6.0; N, 6.0%).

I.r. (KBr) 3160 (NH); 3180, 3072, 3020 (aromatic C-H); 2920, 2845 (NH); 1628 (NH); 1575 ( $\nu$ (OCO)<sub>asym</sub>, unidentate); 1495; 1450; 1375; 1320 ( $\nu$ (OCO)<sub>sym</sub>, unidentate), 1178; 1140; 1015; 842; 743 (mono- and 1,2-di-substituted benzene), 696, 618, 530 (monosubstituted benzene), 440 (1,2-disubstituted benzene).

<sup>1</sup>H n.m.r.  $\delta$  (CDCl<sub>3</sub>, 90 MHz), 1·80, s, 6H, trans O<sub>2</sub>CMe; 2·24, s, 6H, NMe<sub>2</sub>; 2·48, s, 3H, Me; 3·50, s, 2H, benzylic CH<sub>2</sub>; 6·85, b (obscured), 2H, NH<sub>2</sub>; 7·12, s, 4H, aromatic (o-toluidine); 7·36, m, 3H, m, p-aromatic (N,N-dimethylbenzylamine); 7·90, m, 2H, o-aromatic (N,N-dimethylbenzylamine). (400 MHz) 1·82, s, 6H, trans O<sub>2</sub>CMe; 2·28, s, 6H, NMe<sub>2</sub>; 2·48, s, 3H, Me; 3·50, s, 2H, benzylic-CH<sub>2</sub>; 7·14m, 4H, aromatic (o-toluidine); 7·29, s (broad), 2H, NH<sub>2</sub>; 7·40, m, 3H, m, p-aromatic and 7·92, m, 2H o-aromatic (N,N-dimethylbenzylamine).

#### <sup>1</sup>H N.M.R. Studies on Complex Formation at 400 MHz

Lithium tetrachloropalladate (0.1 g) was dissolved in  $D_2O$   $(1 \text{ cm}^3)$  and the solvent removed in a vacuum. The process was repreated thee times and the solid dried at 100° for 2 h after which the H<sub>2</sub>O peak in the <sup>1</sup>H n.m.r. spectrum (60 MHz) was negligible. *N*,*N*-Dimethylbenzylamine (60 mg, 0.45 mmol) and lithium tetrachloropalladate (0.12 g, 0.45 mmol) were mixed in (<sup>2</sup>H<sub>4</sub>)methanol (approx. 0.4 cm<sup>3</sup>) and the spectra run. *N*,*N*-Dimethylbenzylamine (0.06, 0.45 mmol) and palladium diacetate (0.1 g, 0.45 mmol) were mixed in CDCl<sub>3</sub> (approx. 0.4 cm<sup>3</sup>) and the spectra run. Spectra were obtained after five 1-s pulses accumulated 30 s after mixing the reactants and thereafter every 30 s following the 5-s accumulation.

#### Crystallography

Crystal data.—[Pd(NH<sub>2</sub>CH<sub>2</sub>Ph)<sub>4</sub>] [Cl] [O<sub>2</sub>CMe], C<sub>30</sub>H<sub>39</sub>ClN<sub>4</sub>O<sub>2</sub>Pd, M 629 53, triclinic, a 10 · 242(4), b 11 · 378(4), c 14 · 392(4) Å,  $\alpha$  109 · 50(4),  $\beta$  94 · 77(3),  $\gamma$  100 · 01(4), U 1538 · 9 Å<sup>3</sup>, space group P I, Z 2, D<sub>c</sub> 1 · 36 g cm<sup>-3</sup> (D<sub>m</sub> not measured), F(000) 652,  $\mu$  (Mo K $\alpha$ ) 61 · 15 cm<sup>-1</sup>.

Data collection.—CAD4 diffractometer, Zr filtered Mo K $\alpha$  radiation ( $\lambda 0.71073$  Å),  $\omega - 2\theta$  scan mode,  $\omega$  scan width =  $1.0+0.35 \tan \theta$ , scan speed  $1.54-6.77^{\circ} \min^{-1}$ , 3539 data measured, 2321 observed ( $I > 3\sigma(I)$ ). Data were corrected for absorption. Crystals were plates of poor quality.

Structure determination and refinement.—Heavy atom method, full-matrix least-squares. Nonhydrogen atoms assigned anisotropic temperature factors, hydrogens isotropic (a single overall value). The final R and  $R_w$  values are 0.084 and 0.095, weighting scheme  $w = 1/\sigma(F_0)^2$ . All computations were carried out with program Shelex and scattering factors were taken from ref.<sup>23</sup> Tables of thermal parameters and lists of  $F_0/F_c$  values have been deposited as Supplementary Publication with the Editor-in-Chief, Editorial and Publications Service, CSIRO, 314 Albert Street, East Melbourne, Vic. 3002.

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<sup>23</sup> Ibers, J. A., and Hamilton, W. C., (Eds), 'International Tables for X-Ray Crystallography' Vol. 4,
p. 99 (Kynoch Press: Birmingham 1974).