

# Reaction of Tertiary Amines with Bis(benzonitrile)dichloropalladium(II). Formation and Crystal Structure Analysis of Di- $\mu$ -chloro-dichlorobis[2-(*N,N*-di-isopropyliminio)ethyl-C]dipalladium(II)

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Reaction of  $\text{PdCl}_2 \cdot 2\text{PhCN}$  with ethyldi-isopropylamine, tri-*n*-butylamine, or triethylamine at ambient temperature gives good yields of the  $\eta^1$ -ylidic complexes (2)–(5).

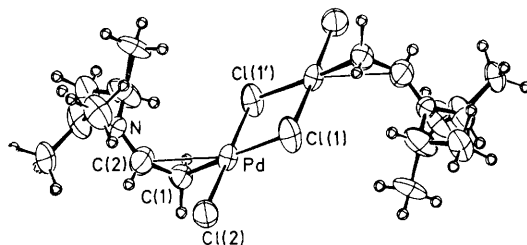
Tertiary amines, such as triethyl- or tri-*n*-butyl-amine, have been very widely used<sup>1</sup> as catalysts in reactions involving palladium(II) species and there appear to be few reports<sup>2</sup> concerning chemical transformations of these amines during the reaction. Recently, however, there have been a number of studies of C–N bond cleavage in tertiary amines involving  $\text{Pd}^0$  or  $\text{Pd}^{\text{II}}$  catalysis, usually at elevated temperatures. Publications have dealt with alkyl exchange<sup>3</sup> at N, hydrolysis<sup>4</sup> to a secondary amine and an aldehyde, reactions giving a secondary amine<sup>5</sup> and a sulphide<sup>6</sup> or selenide,<sup>7</sup> and carbonylation in the presence of organic halides to give<sup>8</sup> tertiary amides. The key step in most of these reactions<sup>3,4,6,7</sup> has been suggested to be the generation of a palladium complex of an iminium ion (1) which then suffers nucleophilic attack. We have found that some tertiary amines react with  $\text{PdCl}_2 \cdot 2\text{PhCN}$  at ambient temperature to give, not simple complexes of iminium ions, but, rather, the products (2)–(5) of further transformation in which palladium is co-ordinated in a  $\eta^1$  fashion to the ylidic form of an enamine.

Reaction of ethyldi-isopropylamine with 1 mol. equiv. of  $\text{PdCl}_2 \cdot 2\text{PhCN}$  in  $\text{CH}_2\text{Cl}_2$  or  $\text{CDCl}_3$  at ambient temperature was essentially complete (t.l.c., <sup>1</sup>H n.m.r.) within 1 h to give  $\text{Pd}^0$  (28%), (2) (17%, m.p. 174–181 °C), (3) (28%, m.p. 146–191 °C, mixture of isomers), and ethyldi-isopropylamine hydrochloride (7%). Similar reactions were achieved with tri-*n*-butylamine during 24 h to give (4) (33%, oil) and with triethylamine during 48 h to give (5) (31%, m.p. 149–153 °C). The addition of small amounts of bis(dibenzylideneacetone)-palladium(0) had no appreciable effect on the rates of these reactions. All four compounds were purified by preparative t.l.c. [some decomposition, especially of (4)] and then (2), (3), and (5) were crystallised to give air-stable, red-brown solids. The structures assigned are consonant with their i.r. and <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra. Thus, for example, (2) has  $\nu(\text{C}=\text{N})$  1613  $\text{cm}^{-1}$  (Nujol); <sup>1</sup>H n.m.r. ( $\text{CDCl}_3$ ),  $\delta$  1.33 (d, 6H,  $\text{CH}_3$ , *J* 6.5 Hz), 1.56 (d, 6H,  $\text{CH}_3$ , *J* 6.5 Hz), 3.31 (d, 2H,  $\text{CH}_2$ , *J* 9 Hz), 3.88 (septet, 1H, N–CH, *J* 6.5 Hz), 4.34 (septet, 1H, N–CH, *J* 6.5 Hz), and 7.81 (t, 1H, N=CH, *J* 9 Hz); <sup>13</sup>C(<sup>1</sup>H-decoupled) n.m.r. resonances at 17.45 ( $\text{CH}_2$ ), 19.16 ( $2 \times \text{CH}_3$ ), 23.04 ( $2 \times \text{CH}_3$ ), 50.74 (C–N), 52.45 (C–N), and 164.92 p.p.m. (C=N). The structure was confirmed by an X-ray crystallographic study (see Figure 1). The molecule occurs as a centrosymmetric dimer with the unique Pd atom having slightly distorted

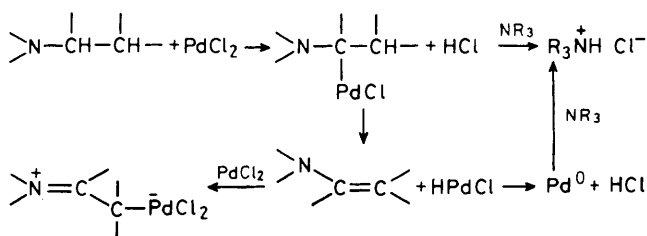
square-planar co-ordination. A noteworthy feature of the structure is the interaction of the carbon [C(2)] of the C=N moiety with the Pd atom [ $\text{Pd} \cdots \text{C}(2)$  2.705(9) Å,  $\text{Pd}-\text{C}(1)-\text{C}(2)$  101.0(6)°]. We have observed<sup>9</sup> a slightly greater distortion ( $\angle \text{Pd}-\text{C}-\text{C}$  ca. 98°) away from the tetrahedral valence angle in 2-oxoalkylpalladium complexes although no such effect is apparent<sup>10</sup> in some  $\alpha$ -cyanopalladium derivatives ( $\angle \text{Pd}-\text{C}-\text{C}$  108–114°).

*Crystal data:*  $\text{C}_{16}\text{H}_{34}\text{Cl}_4\text{N}_2\text{Pd}_2$ ,  $M_r = 609.1$ , orthorhombic,  $a = 13.914(2)$ ,  $b = 12.017(2)$ ,  $c = 14.010(2)$  Å,  $U = 2342.3$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.73$  g  $\text{cm}^{-3}$ ,  $F(000) = 1216$ ,  $\mu(\text{Mo}-K\alpha) = 19.8$   $\text{cm}^{-1}$ . Space group *Pbca* determined uniquely from the systematic absences. Anisotropic refinement of the non-hydrogen atoms, with hydrogen atoms in geometrically idealised positions, converged† with  $R = 0.039$  and  $R_w = 0.040$  for 1141 reflections with  $I > 3\sigma(I)$  and  $2 < \theta < 27^\circ$  measured on a CAD-4 diffractometer.

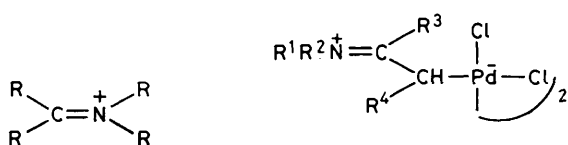
A plausible mechanism (see Scheme 1) for the formation of these enamine complexes involves complexation of palladium



**Figure 1.** A view of the molecule (2). Principal dimensions are:  $\text{Pd}-\text{Cl}(1)$  2.444(2),  $\text{Pd}-\text{Cl}(1')$  2.331(3),  $\text{Pd}-\text{Cl}(2)$  2.299(3),  $\text{Pd}-\text{C}(1)$  2.047(9),  $\text{Pd} \cdots \text{C}(2)$  2.705(9),  $\text{C}(1)-\text{C}(2)$  1.422(13),  $\text{C}(2)=\text{N}$  1.249(12) Å,  $\angle \text{Pd}-\text{C}(1)-\text{C}(2)$  101.0(6),  $\text{C}(1)-\text{C}(2)=\text{N}$  136.0(10)°. Atom C(1) lies 0.146 Å below and C(2) 1.170 Å above the Pd, Cl(1), Cl(1'), Cl(2) plane. Cl(1') is generated from Cl(1) by operation of the symmetry transformation  $-x, -y, -z$ .



**Scheme 1**



- (1)  $\text{R}^1 = \text{R}^2 = \text{Pr}^i$ ,  $\text{R}^3 = \text{R}^4 = \text{H}$   
 (2)  $\text{R}^1 = \text{Et}$ ,  $\text{R}^2 = \text{Pr}^i$ ,  $\text{R}^3 = \text{Me}$ ,  $\text{R}^4 = \text{H}$   
 (3)  $\text{R}^1 = \text{R}^2 = \text{Bu}^n$ ,  $\text{R}^3 = \text{H}$ ,  $\text{R}^4 = \text{Et}$   
 (4)  $\text{R}^1 = \text{R}^2 = \text{Et}$ ,  $\text{R}^3 = \text{R}^4 = \text{H}$

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

to the nitrogen atom followed by metal insertion into the adjacent C-H bond, and then  $\beta$ -hydride elimination to give the enamine which complexes to PdCl<sub>2</sub>. (An alternative mechanism, involving an initial insertion of *N*-complexed palladium into a  $\beta$ - rather than an  $\alpha$ -C-H bond, appears unlikely since the former process<sup>11</sup> should be much less favourable than the latter.<sup>4,12</sup>) Complexes of enamines with Pd<sup>II</sup> have been postulated as reaction intermediates<sup>2,4</sup> and air-stable Pt<sup>II</sup> complexes of enamines have been prepared<sup>13</sup> recently by direct reaction with Zeise's dimer.

Although compounds (2)–(5) are reasonably stable, as solids or in neutral solutions, they do decompose slowly in CH<sub>2</sub>Cl<sub>2</sub> containing pyridine and traces of water to give the appropriate simple aldehyde or ketone presumably *via* hydrolysis to the  $\beta$ -oxoalkylpalladium species which then suffers Pd-C bond cleavage by the HCl formed. We are presently investigating this and other reactions of complexes (2)–(5) as well as the products of reaction of Pd<sup>II</sup> derivatives with a further group of tertiary amines.

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