In memory of S. M. Nelson

Preparation, Nuclear Magnetic Resonance Spectra, and *X*-Ray Diffraction Study† of Bis(*N*-benzylacetimidic acid ethyl ester)dichloropalladium(II)

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N-Benzylacetimidic acid ethyl ester (L) yields a stable complex of the type *trans*-$[PdCl_2L_2]$ with the nitrogen atoms as σ donors. This is not readily convertible to an *ortho*-palladated complex. An *X*-ray crystallographic study reveals a centrosymmetric structure [monoclinic, space group $P2_1/c$, $a = 9.983(4)$, $b = 9.492(23)$, $c = 14.111(10)$ Å, $\beta = 114.02(4)°$, and $Z = 2$]. Splitting of the ^1H n.m.r. signal corresponding to the $CH_3C=$ group is attributed to the presence of two slowly interconverting rotamers (probably about the Pd–N bond), while a more rapid fluxional mode must be responsible for the temperature variation in the chemical shift of the CH_2O groups.

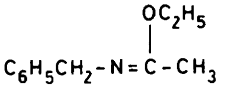
As one of a range of ligands expected to undergo synthetically useful insertion reactions (*cf.*[1]) we sought to prepare an *ortho*-palladated complex from *N*-benzylacetimidic acid ethyl ester[2,3] (L). However, all conditions tried led only to the *N*-bonded complex $[PdCl_2L_2]$ and treatment with base failed to eliminate hydrogen chloride from this to yield the desired metallated compound.

Results and Discussion

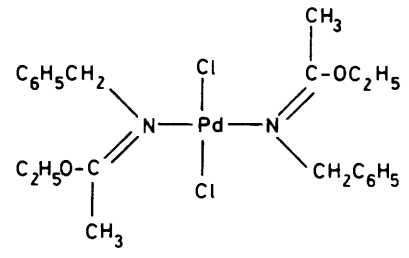
Examination of the ^1H n.m.r. spectrum of $[PdCl_2L_2]$ surprisingly revealed two signals corresponding to the methyl group of the acetimido residue (CH_3–C=) at δ 2.27 and 2.64 p.p.m. (in $CD_3C_6D_5$ at 293 K). These were broad at room temperature, sharp at 243 K, and collapsed to a singlet above 333 K; the coalescence point was 325 K. A significant, if smaller, change of the signals due to the methylene moiety of the benzyl group occurred at the same time. We believe that these changes are best explained by the presence in solution of two rotamers which only interconvert slowly at the lower temperatures. A separate process affects the signal due to the CH_2 moiety of the ethoxy group. This is the expected quartet and remains reasonably sharp over the above temperature range but its chemical shift changes from δ 2.25 at 213 K to δ 3.19 at 373 K, indicating a significant change in the average environment of this group. While remote from benzene rings in the extended conformation revealed by the solid-state structure (see below) use of the molecular graphics program INTERCHEM[4] shows that this methylene group can move into close proximity of the nearer aromatic ring as a result of rotation about the =C–O bond. Such rotation is presumably facile at all accessible temperatures, but the higher energy conformations in which the methylene group is magnetically deshielded by the aromatic system will be populated to an increasing extent as the temperature is raised. In contrast the methyl moiety of the ethoxy groups shows the smaller chemical shift change from δ 0.45 at 213 K to δ 0.60 at 373 K.

Table 1. Selected bond lengths (Å) and angles (°) for $[PdCl_2L_2]$ with estimated standard deviations in parentheses

Pd–Cl	2.3009(12)	C(5)–C(6)	1.507(6)
Pd–N(1)	2.029(3)	C(7)–C(8)	1.405(7)
N(1)–C(1)	1.280(5)	C(7)–C(6)	1.377(6)
N(1)–C(5)	1.481(5)	C(8)–C(9)	1.363(8)
O(1)–C(1)	1.317(5)	C(9)–C(10)	1.383(8)
O(1)–C(3)	1.474(7)	C(10)–C(11)	1.373(8)
C(1)–C(2)	1.497(6)	C(11)–C(6)	1.403(6)
C(3)–C(4)	1.479(9)		
Cl–Pd–N(1)	88.47(10)	N(1)–C(5)–C(6)	114.4(3)
Pd–N(1)–C(1)	124.9(3)	C(8)–C(7)–C(6)	119.9(4)
Pd–N(1)–C(5)	116.55(25)	C(7)–C(8)–C(9)	120.2(5)
C(1)–N(1)–C(5)	118.3(3)	C(8)–C(9)–C(10)	120.5(5)
C(1)–O(1)–C(3)	121.5(4)	C(9)–C(10)–C(11)	119.8(5)
N(1)–C(1)–O(1)	117.9(4)	C(10)–C(11)–C(6)	120.8(5)
N(1)–C(1)–C(2)	122.1(4)	C(5)–C(6)–C(7)	124.4(4)
O(1)–C(1)–C(2)	120.0(4)	C(5)–C(6)–C(11)	116.7(4)
C(1)–C(3)–C(4)	108.0(5)	C(7)–C(6)–C(11)	118.9(4)


$C_6H_5CH_2-N=\overset{\displaystyle OC_2H_5}{\overset{|}{C}}-CH_3$

L



$[PdCl_2L_2]$

To ascertain that the spectral behaviour described above is not due to unexpected structural features, possibly even agostic bonding[5] of a methyl group to palladium, a crystallographic study was undertaken. This did not reveal any interactions which would lead us to alternative explanations.

Single-crystal X-*Ray Structure Determination.*—The yellow crystals of $[PdCl_2L_2]$ are monoclinic, space group $P2_1/c$ with $Z = 2$, *i.e.* the palladium atom is on the centre of inversion and the molecule is therefore centrosymmetric with the Pd, N, and C atoms perfectly coplanar. Selected bond distances and angles are given in Table 1. Atomic co-ordinates are listed in Table 2. The Figure shows a projection of the molecule.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.

Table 2. Final fractional atomic co-ordinates for $[PdCl_2L_2]$ with estimated standard deviations in parentheses

Atom	x	y	z
Pd	0.000 00	0.000 0	0.000 00
Cl	0.116 02(12)	0.136 88(11)	−0.078 84(9)
N(1)	0.132 5(4)	−0.163 5(3)	0.000 73(24)
O(1)	0.193 0(3)	−0.365 3(3)	−0.053 62(25)
C(1)	0.093 2(4)	−0.269 5(4)	−0.061 3(3)
C(2)	−0.061 3(5)	−0.287 7(5)	−0.139 5(4)
C(3)	0.163 4(6)	−0.479 2(5)	−0.131 0(5)
C(4)	0.304 8(7)	−0.547 3(7)	−0.114 5(6)
C(5)	0.289 5(4)	−0.150 0(4)	0.071 5(3)
C(7)	0.239 0(5)	−0.310 6(4)	0.198 9(3)
C(8)	0.290 5(6)	−0.379 2(5)	0.295 5(4)
C(9)	0.433 1(6)	−0.364 1(6)	0.363 8(4)
C(10)	0.527 8(6)	−0.279 5(7)	0.339 3(4)
C(11)	0.478 4(5)	−0.212 2(6)	0.244 9(4)
C(6)	0.332 8(4)	−0.228 1(4)	0.172 8(3)

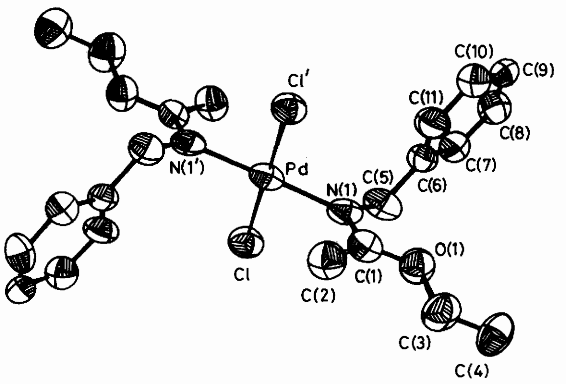

Figure. Molecular structure of *trans*-$[PdCl_2L_2]$

Experimental

Preparation.—Palladium chloride (0.50 g, 2.82 mmol), *N*-benzylacetimidic acid ethyl ester[2,3] (0.55 g, 3.10 mmol), and sodium acetate (0.23 g, 2.82 mmol) were stirred in ethanol (20 cm^3) for 2 h at 60 °C. During this time all the palladium chloride dissolved and a small amount of black precipitate formed which was filtered off. Dilution with water (20 cm^3) then precipitated the yellow product $[PdCl_2L_2]$ (340 mg, 41%) which was collected and recrystallised from ethanol, m.p. 158 °C (Found: C, 49.3; H, 5.75; Cl, 13.8; N, 5.4. $C_{22}H_{30}Cl_2N_2O_2Pd$ requires C, 49.7; H, 5.7; Cl, 13.3; N, 5.3%). ^1H N.m.r.: ($CDCl_3$, 293 K), δ 7.60—7.19 (m, 10 H, ring H), 4.39 (s, 4 H, CH_2–N), 4.06 (q, 4 H, J 7 Hz, CH_2O), 2.48 [2.97] (6 H, br s, =C–CH_3), and 1.22 p.p.m. (t, 6 H, CH_3CH_2); ($CD_3C_6D_5$, 233 K), δ 7.95 [7.86] and 7.40 [7.37] (2:3, ring H), 4.75 [4.66] (CH_2–N), 2.46 (CH_2O), 2.17 [2.59] (=C–CH_3), and 0.47 p.p.m. (CH_3CH_2) [where the δ values in square brackets represent the minor rotamer (see text, 20—25%)]. ^{13}C N.m.r. ($CDCl_3$): δ 14.32 (CH_3CH_2), 20.17 (CH_3–C=), 53.94 (CH_2O), 66.31 (CH_2N), 127—130.6 (ring, C^{2-6}), 137.5 (ring, C^1), and 166.2 p.p.m. (C=N). [The free ligand shows these peaks at δ 14.38 (CH_3CH_2), 15.17 (CH_3C=), 52.84 (CH_2O), 60.61 (CH_2N), 126.68, 127.47 and 128.62 (ring, C^{2-6}), 141.54 (ring C^1), and 162.29 p.p.m. (C=N).]

X-*Ray Structure Determination.*—*Crystal data.* $C_{22}H_{30}Cl_2N_2O_2Pd$, $M = 531.8$, monoclinic, $a = 9.983(4)$, $b = 9.492(23)$, $c = 14.111(10)$ Å, $\beta = 114.02(4)°$, $U = 1\,213.3$ Å^3 (by least-squares refinement of 25 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P2_1/c$ (no. 14), $Z = 2$, $D_c = 1.455$ g cm^{-3}, μ(Mo-K_α) = 9.86 cm^{-1}, and $F(000) = 544$. Crystal dimensions: *ca.* 0.2 × 0.2 × 0.4 mm.

Data collection and processing. The intensity data were collected on a CAD4 diffractomer in the ω—2θ mode with ω scan width = 0.85 + 0.35 tan θ and ω scan speed 1.5—6.7° min^{-1} using graphite-monochromated Mo-K_α radiation. Of the 3 856 reflections measured ($1.0 \leqslant \theta \leqslant 30.0°$; $\pm h$, $+k$, $+l$), 3 515 were unique. After data reduction 2 255 had $I > 2.5\sigma(I)$ and were used subsequently in structure solution and refinement. No corrections were applied for either absorption or crystal decay.

Structure analysis and refinement. The central Pd atom was located by Patterson methods (SHELX 84)[6] on the inversion centre at the origin (0, 0, 0). Subsequent application of direct methods to the difference structure factors using the DIRDIF[7] procedure revealed the locations of the remaining non-hydrogen atoms for the unique half of the complex. Full-matrix least-squares refinement (SHELX 76)[8] with all non-hydrogen atoms anisotropic and the hydrogen atoms in calculated positions with a fixed thermal parameter (U_{iso} = 0.10 Å^2) gave final discrepancy factors of $R = 0.037$ and $R' = 0.060$, where $w^{-1} = [\sigma^2(F) + 0.005\,369(F)^2]$. The final difference Fourier map contained no features greater than ±0.43 e Å^{-3}; general background level was *ca.* ±0.15 e Å^{-3}.

Acknowledgements

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