

SYNTHESIS, STRUCTURAL CHARACTERIZATION AND CATALYTIC CARBONYLATION OF NITROBENZENE AND AMINES BY MONONUCLEAR PALLADIUM(II) COMPLEXES CONTAINING SUBSTITUTED PYRIDINE LIGANDS

S. B. HALLIGUDI*†, K. N. BHATT†, N. H. KHAN, R. I. KURASHY* and K. VENKATSUBRAMANIAN‡

Catalysis Group† and Synthesis and Structural Chemistry Group, Central Salt and Marine Chemicals Research Institute, Bhavnager 364 002, India

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Abstract—Reaction of 2,6-lutidine and 3-picoline with $\text{pd}(\text{CH}_3\text{COO})_2$ in dry benzene gave diacetato-bis-2,6-lutidine palladium(II) (**1**) and diacetato bis-3-picoline palladium(II) (**2**) respectively. The complexes **1** and **2** were characterized by spectroscopic (IR, UV-Vis, ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR) and structural determination by single crystal X-ray methods. Both the complexes are nearly perfect square planar (*trans*) complexes, the coordination valencies being provided by one of the oxygens of two acetate ligands and the nitrogen of the pyridine. The structure of complex **1** is held by van der Waal's contacts only and the structure of complex **2** is held in space by intermolecular hydrogen bonding. The near identical bond length of Pd—O and Pd—N show that the acetate groups are labile, which may be a principle factor for the catalytic activity of the complexes. Cyclic voltametry studies exhibit an irreversible one electron oxidation with $\Delta E_{\text{pa}} = +0.93$ and $+0.86$ V vs Ag/AgCl. The complexes **1** and **2** with cocatalysts FeCl_3 or CuCl_2 were found to be active homogeneous catalysts in the carbonylation of nitrobenzene to phenylurethane and carbonylation of aromatic and aliphatic amines to diureas respectively in the temperature range 150–200°C and 40 atm. CO, respectively. The catalytic studies indicated that complex **2** was more active than **1** in carbonylation of nitrobenzene and of amines under the reaction conditions studied. In the case of amines, the activities of complex **1** and **2** were decreased in the order *n*-butylamine > diethylamine > benzylamine > cyclohexylamine. However, both complexes were inactive in carbonylation of triethylamine.

Amines are probably the most widespread σ -donor ligands in inorganic coordination compounds and also occur frequently in organometallic complexes.¹⁻⁴ Further, many biological molecules contain amine functional group and also bind to metals in both enzymes and purely synthetic molecules.⁵ Metal amine complexes have received much attention in recent years as reactive models for catalytic hydrodenitrogenation (HDN)⁶ and the study

of their physical properties has also been the subject of great interest for structural features of these complexes.⁷

The literature survey indicates that palladium acetate exists as a trimer in the crystalline state and has a water of crystallization, which curiously is not involved in hydrogen bonding with any of the acetate. Crystals of the acetate crystallized from benzene as well as dichloromethane also contain the trimeric unit.⁸⁻¹⁰ Crystals of derivatives of the acetate ion with palladium have also been investigated by Russian scientists¹¹ who have found that the methyl acetate crystallizes as a trimer and the

* Authors to whom correspondence should be addressed.

† In memory of the crystallographer.

trifluoroacetate as a hexamer. Incidentally, these complexes do not have any solvent of crystallization and the structures are held in space only by conglomerate formation. The average Pd—O distance in these structures is around 1.98 Å. It is interesting to know that no monomeric acetate of the palladium derivatives have been so far subjected to X-ray analysis. This will be discussed later.

Catalytic applications of Pd^{II} complexes especially containing substituted pyridine ligands in carbonylation reactions involving nitro and amine substrates are well known in the literature.^{12–18} However, the data on the effects of substituted pyridine ligands in the catalytic carbonylation reactions is scarce. PdCl₂, with a cocatalyst of CuCl₂, has proved to be a potential catalyst system for Wacker's process of the preparation of acetaldehyde via oxidation of ethylene.¹⁹ The drawback of the Pd^{II} catalyst systems lies in the fact that these systems undergo easy reduction to Pd⁰ during the catalytic reactions^{20,21} and hence need a cocatalyst for the reoxidation of Pd⁰ to Pd^{II}.

Palladium(II) complexes have versatile catalytic activities under homogeneous reaction conditions and it was thought worthwhile to derive correlations between the catalytic activities and structural features of these complexes. In particular, we were interested in the reductive carbonylation of nitrobenzene to phenylurethane and carbonylation of amines such as benzylamine, cyclohexylamine, butylamine and diethylamine to give corresponding diureas under milder reaction conditions of pressures and temperatures, because of their importance in the chemical industry.

EXPERIMENTAL

Pd(CH₃COO)₂ was prepared by the known method.²² 3-Picoline, 2,6-lutidine (Aldrich) and dry benzene were used.

Catalyst preparation

(a) *trans-Diacetato bis 2,6-lutidine palladium(II)* (**1**). A solution of Pd(CH₃COO)₂ (0.01 mmol) in dry benzene was stirred with 2,6-lutidine (0.02 mmol) for 6–8 h to give a pale yellow solid. The complex was filtered, washed with petroleum ether and recrystallized as a yellow micro-crystalline material in MeOH/CH₂Cl₂, which gave a 58% yield. Found: C, 49.1; H, 5.4; N, 6.3. Calc. for PdC₁₈H₂₄N₂O₄: C, 49.3; H, 5.5; N, 6.4%. IR spectral data (KBr/Nujol mull, cm⁻¹): 3400(m), 2970(m), 3000(m), 1620(s), 1480(s), 1380(s), 1360(s), 1315(s), 1180(s), 1050(s), 700(s), 790(s), 590(m), 410(m). UV–Vis (MeOH): λ_{max} (ε):

347(1194), 297(2498), 337 sh (1343). ¹H NMR (ppm) (EtOD): 7.13, 7.21, (d), 7.65, 7.57(q), 2.40(s), 1.54(s). ¹³C{¹H}NMR (ppm): 179.66, 162.32, 139.66, 123.22, 25.27, 21.45.

(b) *trans-Diacetato bis 3-picoline palladium(II)* (**2**). Reaction of Pd(CH₃COO)₂ (0.01 mmol) in dry benzene with 3-picoline (0.02 mmol) gives a light yellow compound on stirring for 7–9 h. It was filtered, washed with petroleum ether and dried *in vacuo*. Light yellow transparent crystals were obtained in 52% yield after 2 days of slow evaporation in MeOH/CH₂Cl₂. Found: C, 46.8; H, 4.3; N, 6.7. Calc. for PdC₁₆H₂₀N₂O₄: C, 47.0; H, 4.4; N, 6.8%. IR spectral data (KBr/Nujol mull cm⁻¹): 3400(m), 3050(m), 1630(s), 1460(s), 1300(s), 1215(s), 1080(s), 1050(s), 700(s), 720(s), 830(s), 585(m), 415(m), UV–Vis (MeOH): λ_{max} (ε): 246 (2479), 340 Sh(390). ¹H NMR (ppm) EtOD): 8.45, 8.39, 7.85, 7.76, 7.45, 7.39, 7.32, 2.38, 1.78. ¹³C{¹H}NMR (ppm) (MeOH): 180.2, 151.61, 148.87, 140.3, 125.06, 22.2, 17.56.

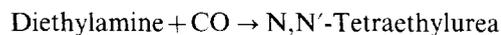
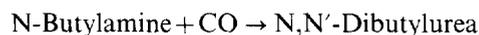
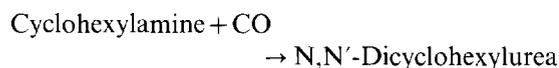
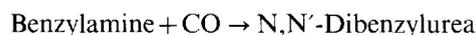
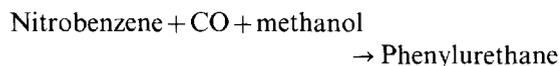
Instrumentation and techniques

Microanalysis of the complexes were performed on a Carlo–Erba analyzer Model 1106. Molar conductance values were obtained at room temperature on a Digisun Electronic Conductivity bridge DI-909. The IR spectra were recorded on Carl Zeiss Specord M-80 spectrophotometer in Nujol mull/KBr. Electronic spectra were recorded on a Shimadzu UV–Vis recording spectrophotometer model 160. ¹H and ¹³C[¹H] NMR spectra were obtained on a Jeol FX-100 NMR spectrometer in deuterated ethanol and methanol using [Si(CH₃)₄] as an internal standard and operating at 99.55 and 24.99 MHz, respectively. Cyclic voltammograms and differential pulse voltammograms were recorded with a Princeton Applied Research (PAR) instrument using tetrabutyl ammonium tetrafluoroborate as a supporting electrolyte in dichloromethane.

Catalytic experiments

Carbonylation experiments were conducted in a 300 cm³ pressure reactor (M/S Parr Instrument Co., U.S.A.) using carbon monoxide gas (purity >99.9%) procured from M/S B.O.C., U.K. In a typical run, a reaction mixture consisting of known amounts of substrate, catalyst and a cocatalyst dissolved in methanol solvent was placed in the reactor. The pressure vessel was flushed twice with nitrogen gas to remove any dissolved gas impurities in the reaction mixture. The vessel was pressurized with the required pressure of CO when the desired

temperature is attained. The sample withdrawn soon after agitation was taken as the zero hour sample and samples withdrawn at different time intervals were analysed for the reactant and the products using a gas chromatograph (Shimadzu G.C 9A, Japan) with an SE-30 column and FID detector. Based on the analysis of reactants and products at different time intervals, conversion (%) and turn over frequencies (TOFs) were calculated. The following reactions were investigated;



X-ray crystallography studies

Crystals of **1** and **2** suitable for X-ray studies were grown by slow evaporation. Yellow plate-like crystals of approximate dimensions $0.17 \times 0.21 \times 0.22 \text{ mm}^3$ and $0.22 \times 0.17 \times 0.21 \text{ mm}^3$ were selected for **1** and **2**, respectively. Intensity data were collected at 2951 K on an Enraf-Nonius CAD-4 diffractometer using $\omega/2\theta$ scans with graphite monochromatized Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$) for **1** and Mo K_α radiation ($\lambda = 0.7107 \text{ \AA}$) for **2**. In each case, the accurate cell dimensions were determined from the least-squares refinement of 25 arbitrarily chosen high-angle reflections.

Crystal decay and orientation during the entire period of data collection was monitored by periodically measuring two sets of three control reflections. Intensities were corrected for Lorentz and polarization factors. Empirical absorption corrections²³ were applied to both data sets using five strong reflections near $\alpha = 90^\circ$ by the Psi scan method. Crystal data for **1** and **2** are given in Table 1. The structures were solved by the heavy atom method; full-matrix least-squares refinement for the isotropic and anisotropic factors using a modified unit-weighting scheme²³ with the Dunitz-Seiler factor²⁴ applied was carried out until convergence was reached. Hydrogen atoms were generated using the known stereochemical constraints or located in the difference map and were given temperature factors based on the atom to which they were connected. Final cycles of full-matrix least-squares refinement with all non-hydrogen atoms (anisotropic) and hydrogen atoms (isotropic, kept fixed), continuing with the same weighting scheme applied, converged

to the final R value of 0.036 ($R_w = 0.038$) for **1** and 0.027 ($R_w = 0.029$) for **2**, respectively. In the last cycle, the shift to the e.s.d. ratio was less than 0.03 and the residual electron density in the final difference map was 0.37 and 0.29 e \AA^{-3} , respectively. All the computations were carried out using the SDP software.²⁵ The scattering factors were from ref. 26. Listing of positional and anisotropic thermal parameters, positions of hydrogen atoms, and F_o/F_c values of both structures are deposited as supplementary material.

RESULTS AND DISCUSSION

The stoichiometric composition of mononuclear Pd^{II} complexes **1** and **2** are consistent with the microanalysis of the complexes. Millimolar solutions of the complexes in methanol are non-electrolytic in nature. The IR spectra of the complexes **1** and **2** show absorption bands around 1480 and 1620 cm^{-1} due to $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$ of 2,6-lutidine or 3-picoline, respectively, and lie at higher wave numbers in the case of the free ligands showing the involvement of ring nitrogen in coordination to the metal ion. The bands observed around 590 cm^{-1} is due to $\nu(\text{M}-\text{N})$.

The UV-vis spectra of the complexes exhibit strong charge transfer bands in the UV range near 346–297 nm of the aromatic nitrogen-containing ligand. The less intense band around 347 nm is attributable to metal–ligand charge transfer absorption.

Complexes **1** and **2** exhibit an irreversible oxidation wave (50 mv s^{-1} with $\Delta E_p = +0.93$ and $+0.86 \text{ v}$ vs Ag/AgCl in tetrabutylammonium tetrafluoroborate in CH_2Cl_2 . Both complexes show no reduction wave up to 1.2 V in CH_2Cl_2 , as reported elsewhere.²⁷ The positive shift in the oxidation potential of complex **1** is due to the weak donor property of 2,6-lutidine because of a steric effect, compared with 3-picoline.

The ^1H NMR spectrum of complex **1** in deuterated ethanol shows a quartet in the region δ 7.65– δ 7.57 ppm due to the proton H_5 *para* to the lutidine nitrogen and a doublet at δ 7.21 and δ 7.13 ppm is due to the protons (H_4, H_6) *meta* to the nitrogen of the lutidine. The resonance signals of higher energy at δ 2.40(s) and 1.54(s) ppm are due to methyl protons of the acetato group and methyl protons of lutidine. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of complex **1** shows the downfield signal at the position δ 179.66, which is due to the coordinated acetato group and three more signals of higher intensities with δ values of 162.32, 139.66 and 123.22 ppm. These three δ values show three different carbon atoms of lutidine the more downfield C_3 *para* to nitrogen and slightly

Table 1. Crystal data

	1	2
Formula	Pd(C ₁₈ H ₂₄ N ₂ O ₄)	Pd(C ₁₆ H ₂₀ N ₂ O ₄)
Mol. Wt	438.80	408.42
Crystal system, space group	Triclinic, <i>PT</i>	Monoclinic, <i>C2/c</i>
<i>a</i> (Å)	8.406(1)	13.635(1)
<i>b</i> (Å)	8.495(1)	11.895(1)
<i>c</i> (Å)	8.555(1)	11.587(1)
α (°)	90.45(1)	-
β (°)	118.64(1)	100.05(1)
γ (°)	116.45(1)	-
<i>V</i> (Å ³)	460.6(3)	1850.4(5)
<i>Z</i>	1	4
<i>D</i> _{calc} (g cm ⁻³)	1.582	1.474
<i>F</i> (000)	224	832
2θ (°) range	2–140	2–47
μ (cm ⁻¹)	170.41	10.064
No. of data collected	1911	1373
No of data observed	1898	937
$ F_{\text{obs}} > 3\sigma(F_{\text{obs}})$		
Max–min. transmission	1–0.58	1–0.91

upfield (C₄,C₆) *meta* to nitrogen and (C₃,C₇) *ortho* carbons. The two upfield signals at δ 25.27 and 21.45 are of the methyl carbon of the acetato group and lutidine methyl protons, respectively.

In the case of complex **2** the low field resonances at δ 8.45, 8.39, 7.85, 7.76, 7.45, 7.39 and 7.32 ppm are due to picoline ring protons. The singlet at δ 2.38 and 1.78 ppm are due to the protons of the acetato group and the methyl protons of picoline. In ¹³C [¹H] NMR, the lower field signal at δ 180.2 ppm is due to the COO⁻ group of the coordinated acetato group. Four more signals a little upfield from same intensities are due to aromatic carbons of picoline δ 151.61 (C₅), 148.87 (C₂, C₆), 140.3 (C₄) and 125.06 (C₃). These values are consistent with those reported elsewhere.²⁸ In the high field region, the signals at δ 22.2 and 17.56 ppm are due to the methyl carbon of the acetato group and another methyl carbon of picoline.

An ORTEP view of the structure of complex **1** is shown in Fig. 1. Palladium is in a square-planar disposition, the Pd—O and Pd—N distances being 2.031(2) and 2.031(1) Å, respectively (Table 2). These values agree with those reported for the acetato complexes and their derivatives.^{8–10,29–33} Since the metal occupies a centre of symmetry, the *trans* angles are exactly 180.0(0)°. The *cis* angles, however, vary from 88.78(9) to 91.22(9)°, a scan of only 2.5°. Hence, the metal may be thought to have more or less perfect square-planar geometry. The Pd, O₁, O₁', N₁, N₁' core (plane A) is accurately planar by symmetry. Plane B, defining the atoms of

the acetato group and the metal, has a maximum deviation of 0.038(3) Å. Plane C, which defines the atoms of the lutidine ligands and the metal, is also found to be planar within experimental error, the maximum deviation being only 0.051(4) Å. Planes A and B are inclined to each other by 94.45(11)°, 1 and 3 by 74.03(8) Å and 2 and 3 by 88.48(6)°. The small deviation from planarity in the case of the lutidine molecule may be a result of steric factors. The dimensions of the carboxyl moiety of the acetate group [1.295(5), 1.198(7) Å, 124.5(3), 114.3(4), 121.3(4)°] shows that this moiety does not occur as a delocalized group i.e. C=O and C—O distances can be distinguished as such. The distance and the angles in the planar lutidine group compare well with the values found in other lutidine^{34,35} structures.

An ORTEP view of complex **2** is shown in Fig. 2. Palladium is in square-planar disposition, as found for the lutidine compound. The Pd—O and Pd—N distances are found to be 2.015(4) and 2.011(3) Å (Table 3) distinctly shorter than those found for the lutidine complex. These values are in consonance with those reported earlier.^{2,8–10} As found in the case of the lutidine complex, the *trans* angles are exactly 180(0)°, while *cis* angles vary from 89.96(1) to 90.1(1)°, a scan of only 2° showing in this complex. The metal has remarkably a perfect square-planar geometry. Plane A defining Pd, O₁, O₁', N₁, N₁' is also planar by symmetry. Plane B, defining the atoms of the acetate group and the metal, is planar within 0.012(4) Å. Plane C, com-

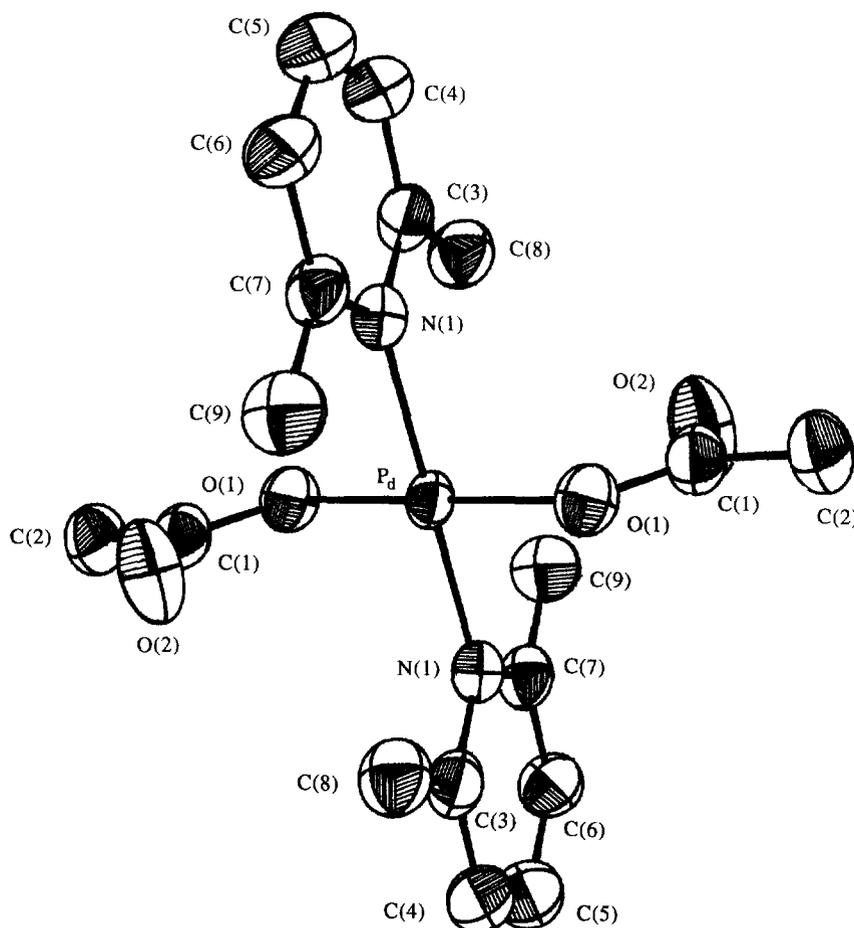


Fig. 1. An ORTEP view of complex 1.

Table 2. Bond distances \AA and angles ($^\circ$) for complex 1

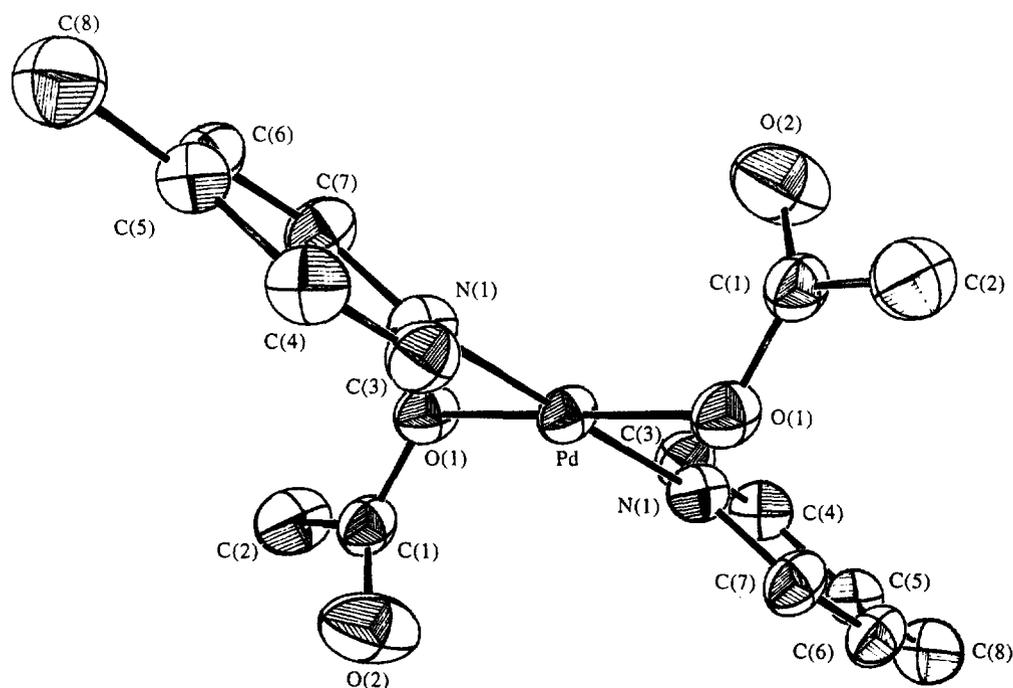
Pd—O(1)	2.031(2)	O(2)—C(1)	1.198(7)	C(3)—C(8)	1.513(6)
Pd—O(1*)	2.031(2)	N(1)—C(3)	1.352(4)	C(4)—C(5)	1.397(8)
Pd—N(1)	2.031(1)	N(1)—C(7)	1.367(4)	C(5)—C(6)	1.385(8)
Pd—N(1*)	2.031(1)	C(1)—C(2)	1.498(5)	C(6)—C(7)	1.392(4)
O(1)—C(1)	1.295(5)	C(3)—C(4)	1.370(3)	C(7)—C(9)	1.467(5)
O(1)—Pd—O(1*)	180.1(5)	Pd—N(1)—C(7)	120.4(2)	C(3)—C(4)—C(5)	119.1(4)
O(1)—Pd—N(1)	91.22(9)	C(3)—N(1)—C(7)	119.1(2)	C(4)—C(5)—C(6)	119.2(3)
O(1)—Pd—N(1*)	88.78(9)	O(1)—C(1)—O(2)	124.5(3)	C(5)—C(6)—C(7)	119.6(4)
O(1*)—Pd—N(1)	88.78(9)	O(1)—C(1)—C(2)	114.3(4)	N(1)—C(7)—C(6)	120.7(4)
O(1*)—Pd—N(1*)	91.22(9)	O(2)—C(1)—C(2)	121.3(4)	N(1)—C(7)—C(9)	118.7(2)
N(1)—Pd—N(1*)	180.1(2)	N(1)—C(3)—C(4)	122.5(4)	C(6)—C(7)—C(9)	120.7(4)
Pd—O(1)—C(1)	116.8(2)	N(1)—C(3)—C(8)	116.7(3)		
Pd—N(1)—C(3)	120.5(2)	C(4)—C(3)—C(8)	120.8(4)		

Numbers in parentheses are estimated standard deviations in the least significant digits.

prising the atoms belonging to 3-picoline and the metal, is planar within $0.015(5)$ \AA . Planes A and B are inclined to each other by $93.32(17)^\circ$, A and C by $48.24(16)^\circ$ and B and C by $93.22(11)^\circ$. The

larger inclination between A and B may be due to steric factors.

The acetate moiety still retains its non-resonating form, since C=O and C—O can be distinguished

Fig. 2. An ORTEP view of complex **2**.Table 3. Bond distances (Å) and angles (°) for complex **2**

Pd—O(1)	2.015(4)	O(2)—C(1A)	1.216(6)	C(3)—C(4)	1.43(1)
Pd—O(1*)	2.015(4)	N(1)—C(2)	1.350(6)	C(4)—C(5)	1.38(1)
Pd—N(1)	2.011(3)	N(1)—C(6)	1.331(7)	C(5)—C(6)	1.388(7)
Pd—N(1*)	2.011(3)	C(1A)—C(2A)	1.524(8)	C(5)—C(7)	1.50(1)
O(1)—C(1A)	1.263(6)	C(2)—C(3)	1.384(9)		
O(1)—Pd—O(1*)	180.0(0)	Pd—N(1)—C(2)	120.6(4)	C(2)—C(3)—C(4)	118.5(6)
O(1)—Pd—N(1)	90.1(1)	Pd—N(1)—C(6)	119.1(3)	C(3)—C(4)—C(5)	120.0(5)
O(1*)—Pd—N(1)	89.9(1)	C(2)—N(1)—C(6)	120.3(4)	C(4)—C(5)—C(6)	117.3(7)
O(1)—Pd—N(1*)	89.9(1)	O(1)—C(1A)—O(2)	127.2(5)	C(4)—C(5)—C(7)	122.4(6)
O(1)—Pd—N(1)	90.1(1)	O(1)—C(1A)—C(2A)	114.1(4)	C(6)—C(5)—C(7)	120.3(6)
N(1)—Pd—N(1*)	180.0(0)	O(2)—C(1A)—C(2A)	118.8(5)	N(1)—C(6)—C(5)	123.3(5)
Pd—O(1)—C(1A)	119.8(3)	N(1)—C(2)—C(3)	120.5(5)		

Numbers in parentheses are estimated standard deviations in the least significant digits.

as such, though to a much smaller degree than in the lutidine complex, as shown by the geometry of the carboxyl group [1.263(6), 1.216(6) Å, 127.2(5), 114.1(4) and 118.8(5)°]. The bond distances and angles in the 3-picoline group compare well with values found for this moiety in other structures.^{36–38}

Although Pd—O and Pd—N distances lie within the range reported, they are more or less indistinguishable. On the basis of atomic radii, M—N bonds are expected to be around 0.05 Å longer

than M—O bonds. The equivalence of these values shows that the acetate groups are more labile. This lability may be the reason for the catalytic activities of these complexes in the carbonylation of nitrobenzene and amines to give their products.

The interaction of the heterocyclic amino ligands presumably breaks down the compact coherent structure of the trimer, which does not have stabilizing hydrogen bonding. Break-down of the primary acetate into monomeric species takes place

Table 4. Activities of palladium(II) complexes along with a FeCl₃ cocatalyst in reductive carbonylation of nitrobenzene to give phenylurethane at 200°C and 40 atm. CO

Catalyst (mmol)	Cocatalyst (gm)	Time (h)	Conversion (%)	TOF ^a
1 (0.23)	1.0	5	37	61
2 (0.25)	1.0	5	61	93

Catalysts: **1**, diacetato-bis-2,6-lutidine palladium(II); **2**, diacetato-bis-3-picoline palladium(II).

Conditions: cocatalyst = FeCl₃, solvent = methanol. Total volume = 100 cm³, substrate (nitrobenzene) = 20 cm³ (0.19 mol).

^aTOF = mole of products per mole of catalyst per h.

initially. This is followed by a change in the ligating nature of the acetate from the bidentate to monodentate mode so that two acetate ions coordinate to palladium to compensate for the charge. The other two unoccupied coordination positions are taken up by the nitrogens of the heterocyclic ligand to form the required complex. However, during the formation of the complex the acetate group becomes labile as mentioned earlier.

In the case of 3-picoline, the structure is held in space by intermolecular interactions between water and acetate through hydrogen bonds from the water molecule. In the case of the lutidine complex **1** there are no short intermolecular contacts and the molecules are held in space only by van der Waal's forces.

The results of reductive carbonylation of nitrobenzene to phenylurethane catalysed by complexes

1 and **2** at 200°C and 40 atm. CO are presented in Table 4. It is seen from the results that complex **1** (TOF = 61) is at least one and half times less reactive than **2** (TOF = 93). The decrease in the catalytic activity of complex **1** could be due to the presence of 2,6-methyl groups (lutidine) in the pyridine ring. Whereas complex **2** has a single 3-methyl (3-picoline) substituted group on pyridine and hence is more reactive than **1** as expected since an increase in the number of substituted methyl group in the pyridine ring decreases its activity in catalytic carbonylation of nitrobenzene due to steric hindrance. The results of carbonylation of benzylamine, cyclohexylamine, butylamine and diethylamine catalysed by complexes **1** and **2** at 150°C and 40 atm. CO to their diureas are presented in Table 5. A comparison of the catalytic activities of **1** and **2** from substrate to substrate shows that complex **1** (TOF = 5.4) is more reactive in the carbonylation of benzylamine than in the case of cyclohexylamine (TOF = 4.7). The decrease in activity of complex **1** in cyclohexylamine could be due to the steric hindrance of the bulky cyclohexyl group. Butyl (primary) and diethyl (secondary) amines show the same trend. Complex **1** is more active in the carbonylation of butylamine (TOF = 7.9) than diethylamine (TOF = 6.1), which could be rationalized by steric hindrance. However, the compound was not active towards triethylamine as this substrate has no replaceable protons for replacing the acetate group of the complex (shown in Scheme 2), which is required for activity. Although complex **2** shows the same trend towards the carbonylations of respective amines, the reactivities of complex **2** in corresponding substrates are marginally higher than that of complex **1**, which

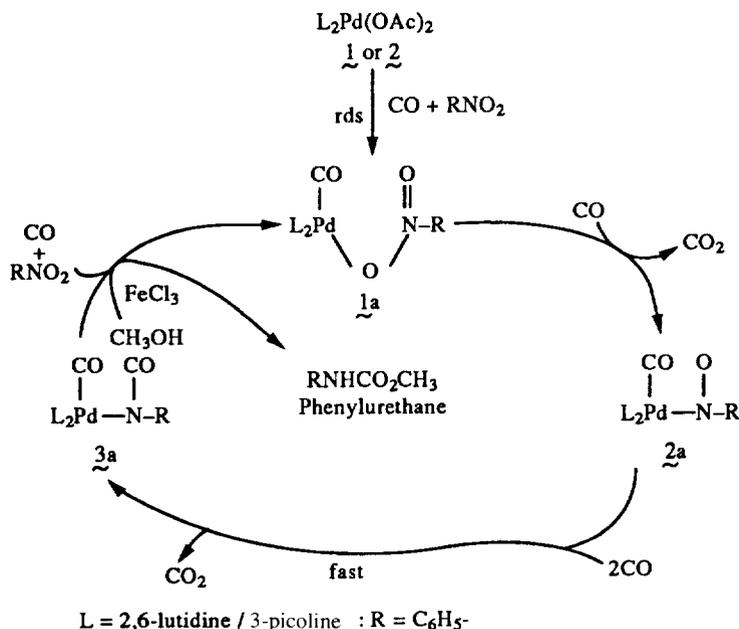
Table 5. Activities of palladium(II) complexes along with CuCl₂ cocatalyst in carbonylation of amines at 150°C and 40 atm. CO

Substrate (mol)	Time (h)	Catalyst 1		Catalyst 2	
		Conversion (%)	TOF ^a	Conversion (%)	TOF ^a
Benzylamine (0.046)	24	65	5.4	100	7.7
Cyclohexylamine (0.044)	24	59	4.7	57	4.2
n-Butylamine (0.050)	24	88	7.9	100	8.3
Diethylamine (0.048)	24	70	6.1	92	7.4
Triethylamine (0.036)	24	no reaction		no reaction	

Catalysts: **1** diacetato-bis-2,6-lutidine palladium(II); **2** diacetato-bis-3-picoline palladium(II).

Conditions: catalyst conc. Catalyst **1** = 0.23 mmol; Catalyst **2** = 0.25 mmol, cocatalyst CuCl₂ = 1.0 g, solvent = methanol. Total volume = 60 cm³, all substrate conc. = 5 cm³ expressed in moles.

^aTOF = mole of products per mole of catalyst per h.



Scheme 1.

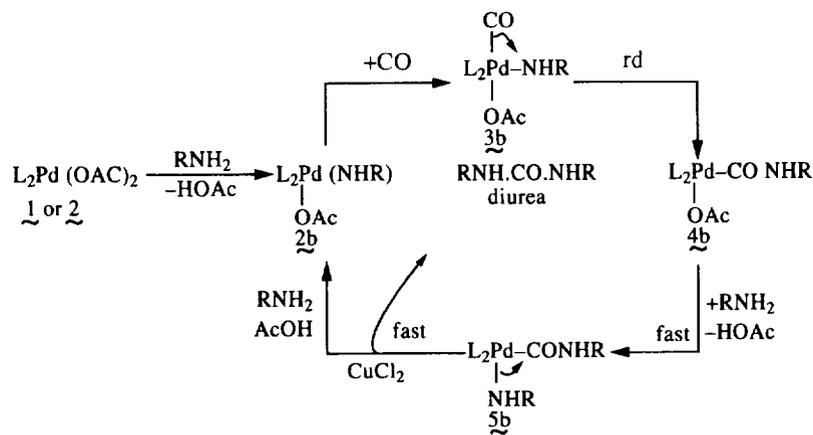
can be attributed to the presence of a singly substituted methyl group in the pyridine ring.

The mechanisms proposed for complexes **1** and **2** catalysed carbonylation of nitrobenzene to phenylurethane and carbonylation of amines are as shown in Schemes 1 and 2, respectively.

Scheme 1 involves the interaction of complex **1** or **2** with CO and RNO₂ to give a mixed-ligand complex (**1a**). In a rate determining step, the mixed-ligand complex **1a** reacts with another molecule of CO forming the nitroso intermediate complex **2a** by deoxygenation of the —NO₂ group of nitrobenzene and the release of CO₂ simultaneously. The nitroso complex **2a** reacts with two more molecules of CO in a fast step to give the phenylisocyanate intermediate complex **3a** via deoxygenation of the nitroso —NO group and simultaneous migration

of CO to the nitrene group. Complex **3a** reacts with methanol in the presence of FeCl₃ cocatalyst to generate the active catalytic species **1a** and phenylurethane.

Scheme 2 involves the activation of the amine by the acetato group of complexes **1** or **2** by the interaction of the acetato ion with H of amine to give HOAc (acetic acid) in the first stage to give the species **2b**. Species **2b** reacts with CO to form a mixed-ligand carbonyl complex **3b**. The insertion of CO into a Pd—N bond to give Pd—CO—NHR will be the rate determining step to give an intermediate species **4b**. Species **4b** reacts with another mole of an amine in a fast step to give species **5b**. Species **5b** in the presence of CuCl₂, RNH₂ and HOAc generate the active catalytic species **2b** and diurea.



Scheme 2.

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