Metal Complexes of *N*-Allylaniline. A Palladium(II) Complex with Co-ordination Number of Greater than Four

By **Michele Aresta,* C. Francesco Nobile,** and **Domenico Petruzzelli,** Istituto di Chimica Generale ed Inorganica, Universita di Bari, Via Amendola, 173, 70126 Bari, Italy
Martin L. Tobe, William Ramsay and Ralph Forster Laboratories, University College, Gower Street, London WC1H OAJ

N-Allylaniline (aa) can act as a uni- or bi-dentate ligand in complexes of composition $[PdCl_2(aa)_2]$ affording an orange-yellow (1) and a dark red isomer (2). The palladium in (1) is four-co-ordinate and planar, with the olefin group unbound in benzene and dimethyl sulphoxide (dmso) solution. The olefin groups in (2) are bound to the palladium, which, in solution (*NN*-dimethylformamide, dmso, or acetone), is at least five-co-ordinate. Both complexes lose methylacetylene and allene to form *trans*-$[PdCl_2(NPhH_2)_2]$ on standing in the solid state or in solution. Isomer (1) requires elevated temperatures and long reaction times, but (2) decomposes readily at room temperature.

As an extension of our previous studies[1] we have investigated the properties of metal complexes of *N*-allylaniline, *NN*-diallylaniline, 2-allylaniline, and 2,6-diallylaniline. In this paper we report the preparation and the chemical and spectroscopic properties of the complexes of palladium(II) with *N*-allylaniline.

RESULTS AND DISCUSSION

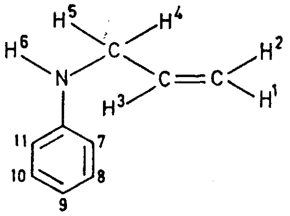
When $[PdCl_2(NCPh)_2]$ was treated with *N*-allylaniline (aa) in benzene solution, a yellow-orange complex analysing as $[PdCl_2(aa)_2]$ (1) was obtained (Table 1). The complex is monomeric in benzene and dimethyl sulphoxide (dmso) and is a non-electrolyte in acetone ($\Lambda = 0.6$ S cm^2 mol^{-1}, [complex] $= 2 \times 10^{-3}$ mol dm^{-3}). The ^1H n.m.r. spectrum in $[^2H_6]$dmso (Table 1) resembled that of the free ligand, except that the signal for the amine proton was absent. The i.r. spectrum of the solid (Nujol mull or KBr disc) contained a strong band at 3 190 cm^{-1} which is assigned to ν(N–H). This shifted to 3 227 cm^{-1} in benzene solution. The corresponding vibration for the free ligand appeared at 3 402 cm^{-1} in the spectrum of a thin film or 3 422 cm^{-1} in the spectrum of a 10^{-2} mol dm^{-3} CCl_4 solution. This shift of frequency is good evidence that the ligand is co-ordinated through the nitrogen. The band at 1 646 cm^{-1} in the free ligand, assigned to ν(C=C), was barely shifted in the spectrum of the complex, although the presence of weak bands at 1 550 cm^{-1} and in the ranges 1 200—1 250 and 900—1 000 cm^{-1} in the spectrum of a Nujol mull suggests that there may be weak interaction between the metal and one of the double bonds in the solid state. The far-i.r. spectrum of a Nujol mull of the complex contained a single band at 562 cm^{-1} assigned to ν(Pd–N) and a sharp band at 335 cm^{-1} assigned to (Pd–Cl).

TABLE 1

Analytical [a] and ^1H n.m.r. data for *N*-allylaniline and its palladium(II) complexes

Compound	Analysis (%) C	H	N	Cl	Pd	Characteristics of the ^1H n.m.r. spectrum [b]
N-Allylaniline $C_9H_{11}N$	81.2 (81.2)	8.35 (8.35)	10.5 (10.5)			2.99 (m, 2 H, $H^{7,11}$), 3.32 (m, 3 H, H^{8-10}), 4.18 (m, 1 H, H^3), 4.37 (sb, 1 H, H^6), 4.79 (dm, 1 H, H^2), 4.93 (dm, 1 H, H^1), 6.37 (dt, 2 H, $H^{4,5}$) [$J(H^1H^3)$ 10.0, $J(H^2H^3)$ 16.8, $J(H^{4,5}H^3)$ 5.0 Hz]
$[PdCl_2(aa)_2]$ (1) $C_{18}H_{22}Cl_2N_2Pd$ (yellow-orange)	49.6 (49.5)	4.90 (5.00)	6.30 (6.30)	16.2 (16.0)	23.15 (23.2)	2.96 and 3.32 (Ph protons), 4.18 (m, 1 H, H^3), 4.80 (d, 1 H, H^2), 4.93 (d, 1 H, H^1), 6.32 (d, 2 H, $H^{4,5}$) [$J(H^1H^3)$ 9.0, $J(H^2H^3)$ 16, $J(H^{4,5}H^3)$ 5.0 Hz]
$[PdCl_2(aa)_2]$ (2) $C_{18}H_{22}Cl_2N_2Pd$ (red)	49.7 (49.5)	4.95 (5.00)	6.30 (6.30)	16.15 (16.0)	23.1 (23.2)	*ca.* 3.10 (m, Ph protons), 3.85 (m, 1 H, H^3), 4.60 (complex pattern, 2 H, $H^{1,2}$), 6.30 (d, 2 H, $H^{4,5}$) [$J(H^{4,5}H^3)$ 7.5 Hz]

[a] Calculated values are given in parentheses. [b] In $[^2H_6]$dmso at 17 °C; τ values with respect to tetramethylsilane (τ 10) as external standard. The protons are numbered as follows:



The diffuse-reflectance spectrum (Table 2) showed maxima at 250 and 350 nm together with a weak broad band centred at 410 nm. The spectrum of a solution in dmso had peaks at 255, 300, and 330 nm and closely resembles that of *trans*-$[PdCl_2(NPhH_2)_2]$, a typical *trans*-square-planar diaminedichloropalladium(II) complex. All these observations are consistent with the

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[1] (*a*) M. Aresta and R. S. Nyholm *Chem., Comm.*, 1971, 1459; (*b*) *J. Organometallic Chem.*, 1973, **56**, 395; (*c*) M. Aresta and G. Vasapollo, *ibid.*, **50**, C51.

formulation of (1) as four-co-ordinate planar *trans*-$[PdCl_2(aa)_2]$ with *N*-allylaniline acting as a unidentate ligand through the nitrogen.

When *N*-allylaniline was allowed to react with $K_2[PdCl_4]$ in water–ethanol (4 : 1) at 0 °C a dark red complex also analysing for $[PdCl_2(aa)_2]$ (Table 1) could be isolated. An identical complex was also obtained, but in much poorer yield, from the reaction between $PdCl_2$ and *N*-allylaniline in acetone at 0 °C. The complex can be stored for long periods at temperatures below −10 °C, but at room temperature it changes slowly into *trans*-$[PdCl_2(NPhH_2)_2]$ and evolves methylacetylene together with a little allene. The reaction is faster in solution and makes the task of characterisation difficult. All the measurements were made on freshly prepared solutions but even with stringent precautions it was not possible to avoid some decomposition.

TABLE 2

Electronic spectra of the complexes[a]

(*i*) Diffuse-reflectance						
(1) (yellow-orange isomer)		250	340	450		
(2) (red isomer)	230	250	360 (sh)			540
[PdCl(tdp)]Cl[b]			365	459	500	
(*ii*) Spectra in 10^{-4} mol dm^{-3} dmso						
(1)		255 (32 700)	300 (12 500)	330 (7 700)		
trans-$[PdCl_2(NPhH_2)]$		250 (24 400)	300 (11 500)	330 (8 100)		
(2)		256 (28 000)	290 (23 000)			434 (3 700)
[PdCl(tdp)]Cl[b]	233 (59 800)	264 (sh)	310 (sh)			454 (6 650)
[Pd(pma)Cl]Cl[c]		262 (16 400)	320 (8 400)			460 (280)

[a] Characteristic peaks, λ/nm; molar absorption coefficients ($\varepsilon/dm^3\,mol^{-1}\,cm^{-1}$) are given in parentheses. [b] tdp = Tris(*o*-diphenylphosphinophenyl)phosphine. Five-co-ordinate trigonal bipyramid with axial chloride in P_4Cl set.[5,6] [c] pma = *o*-Phenylenebis[methyl(*o*-dimethylarsinophenyl)arsine].[7] Five-co-ordinate square pyramidal with basal chlorine in As_4Cl set.[8]

The i.r. spectrum of the red isomer (Nujol mull or KBr disc) contained two bands that can be assigned to ν(N–H) at 3 100 and 3 075 cm^{-1}. (The low solubility prevents the measurement of the i.r. spectrum of a solution.) This shift to lower frequency indicates that the nitrogen is co-ordinated but the magnitude of the shift (>300 cm^{-1}) is larger than that usually observed. For example, Chatt *et al.*[2] showed that, for complexes of the type *trans*-$[PtCl_2(amine)L]$, the shift to lower frequency of ν(N–H) for a variety of primary and secondary amines lies within the range Δν = 100—150 cm^{-1} even though the series of ligands, L, contains a wide variety of Group 5A and 6A donors as well as amines and ethylene. In the range 600—1 700 cm^{-1} the spectrum of the complex differed considerably from that of the free ligand. The band at 1 646 cm^{-1}, assigned to ν(C=C), was absent and two new bands appeared at 1 544 and 1 540 cm^{-1}. These have been assigned to the scissoring mode of the $=CH_2$ group in a π-bonded olefin complex.[3] The out-of-plane bending of the olefinic protons gives rise to bands at 989w, 962m, 942m, 933m, 912m, and 900w cm^{-1}, again diagnostic of a π-olefin complex. [The δ(HCH) vibrations are found at 992s, 977w, and 915s cm^{-1} in the free ligand.] A pair of bands at 523s and 518s cm^{-1}, which are not present in the spectrum of the free ligand, are assigned to ν(Pd–N), the doubling being consistent with a *cis* arrangement of the two amine nitrogens. This can be compared with the two peaks at 561 and 539 cm^{-1} in the spectrum of $[PdCl_2(en)]$ (en = ethylenediamine) and assigned to the coupled ν(Pd–N) vibrations of the *cis*-diamine arrangement.[4] A strong band was also found at 332 cm^{-1} and assigned to ν(Pd–Cl).

The u.v. and visible diffuse-reflectance spectrum of (2) in a MgO mull had maxima at 230, 250, and 530 nm with a shoulder at 360 nm (Table 2). In dmso solution (5 × 10^{-4} mol dm^{-3}) the spectrum changed significantly with maxima at 256, 290, and 434 nm and is similar in some respects to the spectra of known five-co-ordinate complexes of Pd^{II}, for example [PdCl(tdp)]Cl [tdp = tris(*o*-diphenylphosphinophenyl)phosphine] [5] which is trigonal bipyramidal with an axial chlorine,[6] and $[Pd(pma)Cl]^+$ {pma = *o*-phenylenebis[methyl(*o*-dimethylarsinophenyl)-arsine]} [7] which is square pyramidal with a basal chlorine.[8] In view of the relatively small effect of the co-ordination geometry on these spectra, the fact that we are comparing complexes with totally different donor sets, *i.e.* P_4Cl (or As_4Cl) with $N_2(C{=}C)_2Cl$, prevents us from assigning a geometry to the species in solution, although we can be reasonably certain, from the absorption in the blue, that the palladium has a co-ordination number greater than four. The conductance in dmso solution {Λ 23 S cm^2 mol^{-1} (10^{-3} mol dm^{-3} solution); *cf.*[9] 36.3 S cm^2 mol^{-1} for $[NPr^n_4]Cl$} is somewhat less than that expected for a 1 : 1 electrolyte, and even more association is observed in *NN*-dimethylformamide (dmf) (Λ 23 S cm^2 mol^{-1}; normally *ca.* 75 S cm^2 mol^{-1} for 1 : 1 electrolytes) and acetone (Λ 36 S cm^2 mol^{-1}; normally *ca.* 140 S cm^2 mol^{-1} for 1 : 1 electrolytes). This behaviour suggests that the complex might even be six-co-ordinate in the solid state. The ^1H n.m.r. spectrum of a freshly

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prepared solution in [$^2H_6$]dmso suggests that both double bonds are co-ordinated to palladium. This is, to our knowledge, the first example of a palladium(II) complex containing amines and olefins that has a co-ordination number greater than four in solution. The palladium in bis(2-aminopropane-1,3-diamine)palladium(II) iodide is believed to be six-co-ordinate in the solid state,[10] and five-co-ordinate complexes of Pd^{II} containing phosphines, arsines, and stibines are well known. No five-co-ordinate palladium(II) olefin complexes have yet been reported, although those of Rh^I,[11] Ir^I,[12] and Pt^{II} [13] are well known.

Elimination of C_3 *Units*.—When the red isomer (2) is stored at room temperature the colour slowly changes to orange-yellow and the product analyses for [$PdCl_2(NPhH_2)_2$] and is identical to an authentic sample of the *trans* isomer. The conversion was virtually complete in 8 h and gas-chromatographic analysis shows that the volatile part of the product consists of methylacetylene (97%) and allene (3%). In solution the reaction is faster. For example, in dmso at 37 °C the reaction was complete in a few minutes and *trans*-[$PdCl_2(NPhH_2)_2$] and methylacetylene which remained in solution can be identified by characteristic peaks at τ 6.30 (amine protons in the aniline complex) and 8.12 (methyl protons in methylacetylene). An authentic sample of methylacetylene has its methyl resonance at τ 8.12 in dmso (τ 8.20 in CCl_4 and $CDCl_3$). A similar reaction was observed when a suspension of the complex in benzene or toluene was heated. The orange-yellow isomer (1) also gave methylacetylene and allene in the same ratio but much higher temperatures were required.

A number of examples of the elimination of C_3 units from allylammonium salts are reported in the literature. Hawton [14] reported that a mixture of methylacetylene (87%) and allene (13%) is obtained when allyltrimethylammonium hydroxide is heated at 310—325 °C. Pietropaolo *et al.*[15] reported that [$PdCl_4$]$^{2-}$ reacts with diallyl ether in water to give [$\{Pd(\eta\text{-allyl})Cl\}_2$] and acrolein. In our work it is assumed that the isomerisation of the allyl group to propenyl is the first step of the reaction. Isomerisations of this sort, promoted by transition metals such as Mo and Pt, have been observed for analogous ligands such as *o*-allylphenyldiphenylphosphine [16] and *o*-allylphenol.[16] Heck [17] reported that Pd^{II} catalyses the isomerisation of allylbenzene to propenylbenzene. It is unlikely that allene is first formed as an intermediate in our reactions and then isomerises to methylacetylene. Heating of [$\{Pd(\eta\text{-2-chloroallyl})Cl\}_2$] in the presence of triphenylphosphine yields only allene [18,19] with no indication of isomerisation to methylacetylene.

Catalysis of C–N bond cleavage is observed in the palladium(II)-catalysed oxidation of allylamine in the presence of water to give propionaldehyde and MeCOCHO.[20] Rhodium(III) complexes of allylamine (L), [$RhCl_3L(OH_2)$] and [$RhCl_3L_2$], undergo C–N cleavage in the presence of alcohols and water at 50 °C to give a mixture of products such as propionaldehyde, allyl(*N*-propylidene)amine, acrolein, propylene, and other unidentified materials [21] but the reactions are slow. The complex [$RhCl_3L_3$] reacts at 60 °C but only in the presence of HCl. It is suggested that co-ordination of the olefin moiety to the metal is essential for the promotion of bond cleavage. The work reported in this paper provides the only known example so far of a palladium(II)-catalysed cleavage of a C–N bond that takes place rapidly under mild conditions in the absence of water and/or mineral acids. Studies are in progress to elucidate the mechanism of the reaction.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer PE 557 spectrophotometer. Gas-chromatographic analyses were made with a Hewlett–Packard HP 5750 instrument. Hydrogen-1 n.m.r. spectra were obtained with a Varian HA 100 spectrometer. All the reactions were carried out in an atmosphere of pure dry nitrogen. Deuteriated solvents were obtained from J. T. Baker Chemicals.

Preparations.—N-*Allylaniline*. To a vigorously stirred slurry of Na[HCO_3] (85 g, 1 mol) in aniline (93 g, 1 mol) and distilled water (200 cm^3), was added dropwise allyl bromide (120 g, 1 mol) over a period of 1 h while the reaction mixture was maintained at 20 °C. The mixture was then heated under reflux for 1 h, cooled to room temperature, and the organic layer was separated, washed with water, and dried overnight over K[OH]. The pure ligand was separated from the crude product (which also contained aniline and *NN*-diallylaniline) by chromatography over silica gel (1.5-m column, 3-cm internal diameter) using pentane–benzene (4 : 1) as eluant, and was finally distilled (b.p. 72 °C, at 2 mmHg).* Gas-chromatographic analysis (2-m chlorodimethylsilane–Chromosorb column; internal diameter, 3 mm) showed it to be 99.9% pure.

Bis(N-*allylaniline*)*dichloropalladium*(II) (*orange isomer*) (1). The complex [$PdCl_2(NCPh)_2$] (1.0 g 2.6 mmol) dissolved in toluene (30 cm^3) was added dropwise to a stirred solution of *N*-allylaniline (0.70 g, 5.3 mmol) in toluene (30 cm^3). The resulting orange-yellow solution was stirred for another 6 h, then filtered and evaporated *in vacuo* to a volume of 15 cm^3. Careful addition of pentane caused the precipitation of orange crystals, yield 90% based on Pd. The complex darkened at 100 °C and decomposed at 200 °C. Prolonged reaction times resulted in poorer yields and some *trans*-[$PdCl_2(NPhH_2)_2$] was also formed.

Bis(N-*allylaniline*)*dichloropalladium*(II) (*red isomer*) (2). (*a*) A solution of $K_2[PdCl_4]$ (0.50 g, 1.5 mmol) in water (20 cm^3) was added to a stirred solution of *N*-allylaniline (0.41 g,

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

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3 mmol) in air-free ethanol (30 cm^3) at 10 °C. A red product separated and was filtered off as soon as possible, washed with cold water, ethanol, and pentane, and dried at −10 °C. More product could be obtained from the mother liquor but it was generally contaminated with *trans*-$[PdCl_2(NPhH_2)_2]$ and metallic palladium, yield between 30 and 50% based on Pd. The complex became dark yellow at 50 °C and decomposed at 200 °C.

(*b*) *N*-Allylaniline (0.38 g, 2.8 mmol) was added to a slurry of $PdCl_2$ (0.50 g, 2.8 mmol) in acetone (30 cm^3) and the mixture was stirred for 48 h at 0 °C. The resulting red solution was filtered and evaporated to a volume of 5 cm^3. A red complex separated and was filtered off, washed with cold pentane, and dried *in vacuo* at 0 °C. The yield was variable, generally between 5 and 20% based on Pd. The product was often contaminated with *trans*-$[PdCl_2(NPhH_2)_2]$ which was the only product that could be isolated when the reaction was carried out at >10 °C.

Identification of the C_3 *Units*.—The quantitative analysis of the methylacetylene–allene mixture was made using a 4-m succinic acid ester column (internal diameter, 3 mm; 30 °C; carrier gas, N_2; flow rate, 40 cm^3 min^{-1}; flame detector temperature, 150 °C). Pure methylacetylene and allene were used as calibrants. The decomposition of the red and orange isomers was studied using samples (100 mg) contained in a thermostatted cell (5 cm^3) that was connected to the gas-chromatography apparatus through a four-way stopcock. The amount of gas evolved was measured at fixed intervals of time. The conversion of the solid red complex was 99.5% complete (based on the C_3 : Pd ratio) in 2 h at 40 °C and the product consisted of 97% methylacetylene and 3% allene. The orange complex gave the same yield in 2 h but only when the temperature was increased to 90 °C. In dmso solution the decomposition of the red isomer was complete in *ca.* 20 min at 37 °C, and analysis of the gas evolved showed it to be methylacetylene (96%) and allene (4%). The decomposition of the orange complex was also monitored by n.m.r. spectroscopy.

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