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Synthesis and crystal structure of [PdMe{$PPh_2NHC(O)$Me}{O=C(NH_2)Me}][BF_4], a palladium complex containing the acetamide ligand

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Abstract – The synthesis of a square planar cationic Pd(II) complex containing the acetamide ligand is described. The complex has been characterised by X-ray diffraction, leading to one of the rare examples of a crystal structure showing an acetamide molecule coordinated to a metal centre and, to the best of our knowledge, the first one with palladium. This complex may be relevant to catalytic reactions, such as the palladium-catalysed amidocarbonylation, in which transient species with O-coordinated acetamide can be formed. ***To cite this article: P. Braunstein et al., C. R. Chimie 5 (2002) 131–135*** © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

acetamide / acetamidophosphine / crystal structure / palladium

Résumé – Synthèse et structure cristallographique de [PdMe{$PPh_2NHC(O)$Me}{O=C(NH_2)Me}][BF_4], un complexe du palladium comportant le ligand acétamide. Nous décrivons la synthèse d'un complexe cationique du palladium (II) avec le ligand acétamide. Ce complexe a été caractérisé par diffraction des rayons X, conduisant à l'une des rares structures cristallographiques montrant la coordination de $NH_2C(O)Me$ à un centre métallique par l'atome d'oxygène et, à notre connaissance, la première dans le cas de complexes du palladium. Il est probable que des complexes similaires se forment de manière transitoire dans des processus catalytiques impliquant l'acétamide, comme par exemple les réactions d'amidocarbonylation catalysées par des complexes du palladium. ***Pour citer cet article : P. Braunstein et al., C. R. Chimie 5 (2002) 131–135*** © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

acétamide / acétamidophosphine / palladium / structure cristallographique

1. Introduction

The synthesis of polydentate hemilabile ligands, which generally combine a hard and soft donor functionality, is a subject of considerable current interest, in particular with respect to the development of new functional materials and homogeneous catalysts. Numerous metal complexes containing P,O or P,N type ligands are catalytically active in a wide range of reactions of both academic and industrial interest [1–3]. We have recently described a series of cationic Pd(II) complexes, in which the heterofunctional phosphine ligand $Ph_2PNHC(O)Me$ **1** behaves as rigid and/or hemilabile P,O chelate [4]. These complexes were prepared in high yield in a one-pot procedure by reacting **1** with [PdCl(Me)(COD)] (COD = 1,5-cyclooctadiene) and a two-electron donor ligand L, in the presence of a halide abstractor (e.g. $AgBF_4$) in CH_2Cl_2. Interestingly, these complexes could also be obtained by ligand substitution from the acetonitrile

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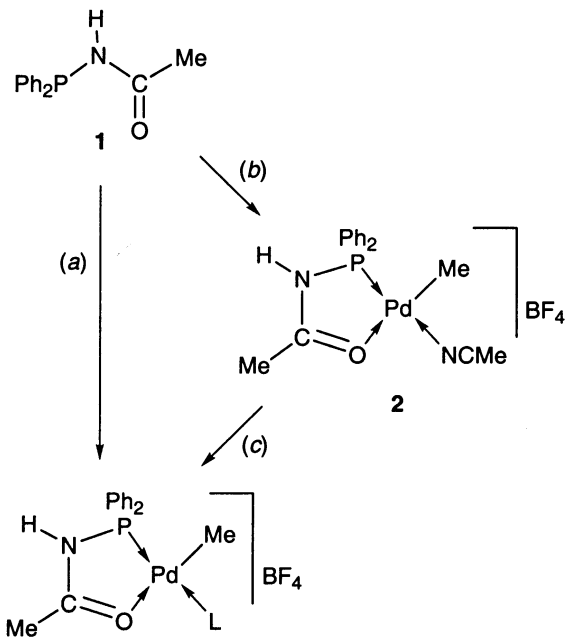
complex **2** by reaction with L (Fig. 1). The chelating ability of **1** was compared to that of other potential P,O chelates. Based on competition experiments, **1** was found to be a stronger chelate than the keto- or amidophosphine ligands $Ph_2PCH_2C(O)Ph$ and $Ph_2PCH_2C(O)NPh_2$, respectively. Thus, in complexes **3** and **4**, these phosphines act as monodentate P ligands, whereas **1** chelates the Pd centre through P and O coordination (Fig. 1).

Furthermore, complex **2** showed a higher stability, both in solution and in the solid state, than its $Ph_2PCH_2C(O)Ph$ analogue, which reflects a greater stabilizing effect of **1**. The dynamic behaviour of the latter in complex **5** evidences the hemilabile properties of this ligand. This led in solution to a fast equilibrium resulting from $Ph_2PNHC(O)Me$ alternatively acting as P,O chelate or P-monodentate ligands [4]. Taking advantage of the stability of this family of complexes, the reactivity of **2** was investigated towards the insertion of CO, ethylene and methylacrylate into the Pd-Me bond, reactions which are of considerable current interest [5–8]. This allowed us to isolate and completely characterise the first intermediates resulting from successive ethylene/CO/methylacrylate coupling, a model system for a terpolymerisation process [9]. During this work, a complex containing acetamide in its coordination sphere was serendipitously obtained, which we describe here. This complex was subsequently prepared in a more rational way.



3 L = $PPh_2CH_2C(O)Ph$
4 L = $PPh_2CH_2C(O)NPh_2$
5 L = $PPh_2NHC(O)Me$
6 L = $O{=}C(NH_2)Me$

Reaction conditions: (*a*) [PdCl(Me)(COD)], L, $AgBF_4$, CH_2Cl_2, RT, -COD, -AgCl;
(*b*) [PdClMe(COD)], $AgBF_4$, MeCN, RT, -COD, -AgCl;
(*c*) L, CH_2Cl_2, RT, -MeCN.

Fig. 1.

2. Results and discussion

The reaction of **1**, [PdCl(Me)(COD)] and methylacrylate in CH_2Cl_2, followed by the addition of $AgBF_4$, afforded after work-up a yellow powder. Its $^{31}P\{^1H\}$ NMR spectrum showed two signals at δ 80.3 and 60.4 ppm (ratio: 2:1), indicating the presence of two products. This was confirmed in the ^1H NMR spectrum, which showed two sets of signals, the methylacrylate remaining apparently unreacted. The structure of the complex to which the ^{31}P resonance at δ 80.3 ppm was ascribed has been determined by X-ray diffraction (Fig. 2). It showed the unexpected formation of the cationic Pd(II) complex **6**, in which the fourth coordination site is occupied by an acetamide ligand, coordinated to the metal centre by the oxygen atom (Fig. 1). This is, to the best of our knowledge (SciFinder search), only the second complex of this type with coordinated acetamide to a Pd centre [10] and the first one to be structurally characterised. This surprising result prompted us to determine the origin of this ligand. Since a similar reaction carried out in the absence of methylacrylate led to the same mixture of products, we could rule out a possible involvement of methylacrylate in the formation of **6**. We therefore came to the conclusion that acetamide arose from partial decomposition (or hydrolysis?) of the phosphine ligand $Ph_2PNHC(O)Me$, after storage for several months in a Schlenk flask. In retrospect, this is not too surprising if one considers that P–N bonds are known to be reactive, as for example in diphosphazanes where the P–N bond is easily cleaved in protic solvents [11].

The $^{31}P\{^1H\}$ NMR resonance at δ 60.4 ppm was ascribed to $[PdMe\{PPh_2NHC(O)Me\}\{PPh_2NHC(O)Me\}][BF_4]$ **5**, which has been previously synthesised and characterised [4]. We have rationalised the synthesis of **6** by carrying out the reactions described in Fig. 1 in the presence of acetamide. The one-pot procedure also led to a mixture of **5** and **6** (ratio: 1/2). This may be due to a competition between non-coordinated **1** and acetamide for the fourth coordination site at Pd. We also verified that once **5** is formed, acetamide is not capable of displac

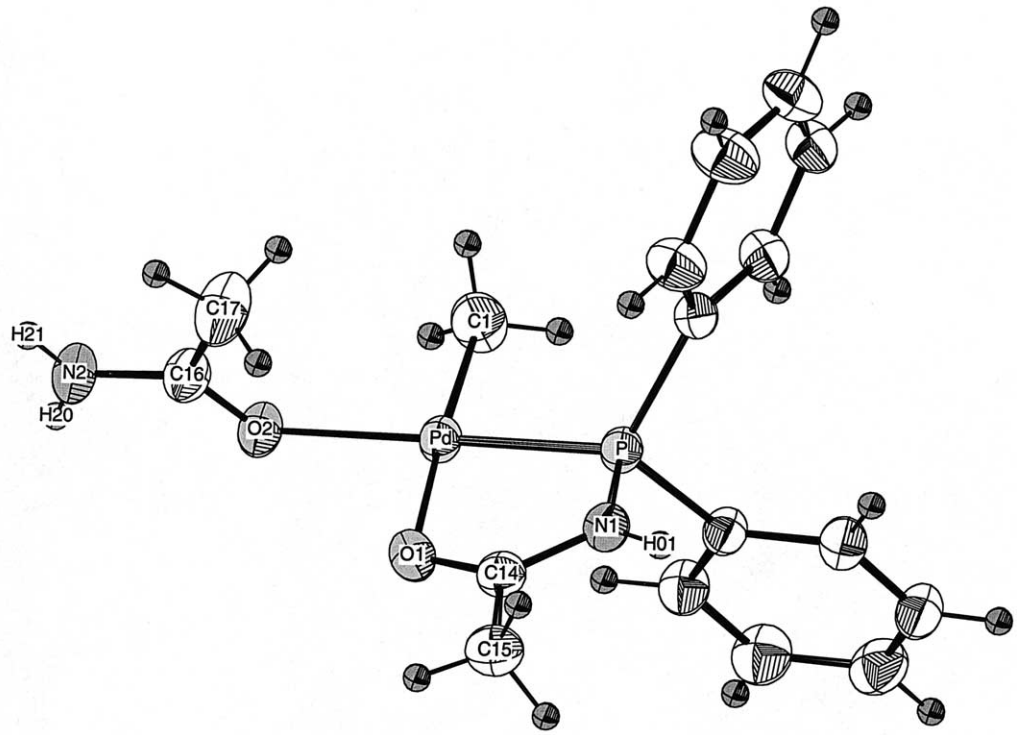


Fig. 2. View of the molecular structure of the cation in **6**·0.5 CH_2Cl_2.

ing the $Ph_2PNHC(O)Me$ ligand in this complex. However, the two-step procedure allowed the synthesis of pure **6** by displacement of the acetonitrile ligand of **2** by acetamide. Complex **6** is rather stable, even in solution, which suggests that compounds of this type may be present in palladium-catalysed reactions such as the amidocarbonylation to form amino acid derivatives [12] or the hydration of nitriles to carboxamides [13].

3. Crystal structure of [P$\overline{dMe\{PPh_2NHC(O}$)Me}{O=C($NH_2$)Me}][$BF_4$]·0.5 CH_2Cl_2

X-ray quality single crystals of **6**·0.5 CH_2Cl_2 were grown by slow diffusion of pentane into a concentrated dichloromethane solution of **6**. The crystals contain 0.5 molecule of dichloromethane per molecule of **6**. The molecular structure of **6** is represented in Figs. 2 and 3. Selected bond lengths and angles are given in Table 1.

The geometry at Pd is square planar, as reflected in the P–Pd–O(2) and C(1)–Pd–O(1) angle values of 177.37(5) and 174.2(1)°, respectively. The four atoms coordinated to Pd, as well as the N(1), C(14) and C(15) atoms of the phosphine ligand, lie in the same plane, which also contains the Pd centre. The bond lengths and angles involving the P,O chelate are within the same range as those found in [P$\overline{dMe\{PPh_2NHC(O}$)Me}{$PPh_2NHC(O)Me$}][$CF_3SO_3$] [4] and in [P$\overline{dMe\{CH_2CH_2C(O}$)Me}{$PPh_2NHC(O)$Me}][$PF_6$] [9]. The acetamide ligand is coordinated to the Pd centre via its oxygen atom [Pd–O(2): 2.120(2) Å] in a *trans* position to the P atom of the P,O ligand. This results in a *cis* arrangement of the two oxygen atoms around the Pd centre [O(1)–Pd–O(2): 94.28(8)°]. The bond distances and angles involving the acetamide ligand are in the expected range and are similar to those found in other complexes containing an acetamide or acetamidate ligand that have been structurally characterized [14–17].

Table 1. Selected bond distances (Å) and angles (°) for **6**·0.5 CH_2Cl_2[a].

Pd–C(1)	2.018(3)	N(1)–C(14)	1.350(3)
Pd–O(2)	2.120(2)	C(14)–O(1)	1.246(3)
Pd–P	2.1558(6)	O(2)–C(16)	1.252(3)
Pd–O(1)	2.170(2)	C(16)–N(2)	1.321(3)
P–N(1)	1.709(2)		
C(1)–Pd–O(2)	90.27(11)	C(14)–N(1)–P	119.6(2)
C(1)–Pd–P	91.88(9)	O(1)–C(14)–N(1)	121.6(2)
O(2)–Pd–P	177.37(5)	C(14)–O(1)–Pd	114.7(2)
C(1)–Pd–O(1)	174.2(1)	C(16)–O(2)–Pd	122.5(2)
O(2)–Pd–O(1)	94.28(8)	O(2)–C(16)–N(2)	120.2(2)
P–Pd–O(1)	83.49(6)		

[a] Estimated standard deviations in the least significant figure are given in parentheses.

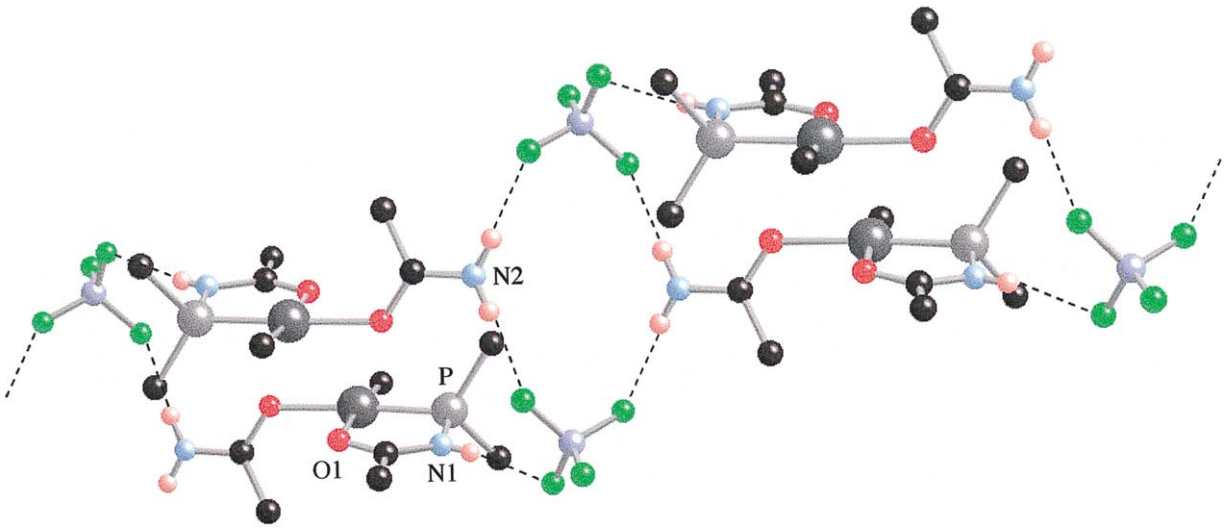


Fig. 3. View of the packing of **6** in **6**·0.5 CH_2Cl_2 showing the 'dimeric' units connected through H···F bonding (see text). Dichloromethane molecules of solvation and phenyl groups, except the ipso carbon atoms, have been omitted for clarity.

In the lattice, molecules of **6**·0.5 CH_2Cl_2 form 'dimeric' units, resulting from a head-to-tail packing with the centre of symmetry on the position ½, 0, 0 of the $P2_1/n$ space group (Fig. 3). In this arrangement, the oxygen atom of the P,O ligand of one molecule lies above the Pd centre of the other molecule at a Pd···O(1) distance of only 3.087 Å. Furthermore, these 'dimeric' units are connected to other 'dimers' via hydrogen bonding involving the N–H protons and the BF_4 anions (Fig. 3) with average H···F separations of 2.1 Å. The centre of symmetry is on the position ½, ½, 0 of the $P2_1/n$ space group.

4. Experimental section

All reactions were performed using Schlenk-tube techniques under dry nitrogen. Solvents were dried and distilled prior to use under nitrogen. The ^1H and $^{31}P\{^1H\}$ spectra were recorded at 300.1 and 121.5 MHz, respectively, on a FT Bruker AC 300 instrument. The $^{13}C\{^1H\}$ NMR spectra were recorded at 50.32 MHz on a FT Bruker AC 200 instrument. IR spectra were recorded in the 400–4000 cm^{-1} range on a Bruker IFS66 FT spectrometer. Elemental C, H and N analyses were performed by the 'Service de microanalyse du CNRS' (ULP, Strasbourg).

4.1. Preparation of [PdMe{$PPh_2NHC(O)$}Me]{O=$C(NH_2)$Me}][BF_4] 6

4.1.1. Method (a)

Solid [PdCl(Me)(COD)] (0.248 g, 0.936 mmol) was added to a solution of $Ph_2PNHC(O)Me$ (0.227 g, 0.936 mmol) in CH_2Cl_2 (75 ml) at ambient temperature. Then acetamide (0.055 g, 0.936 mmol) was added and the mixture was stirred for 30 min before solid $AgBF_4$ (0.182 g, 0.936 mmol) was added. The solution was then stirred for 30 min before it was filtered. The solvent was evaporated under vacuum to leave a yellow solid, which was washed with pentane (10 ml) and diethyl ether (10 ml) and dried under vacuum. The solid that was isolated (0.350 g) consisted in a mixture of **5** and **6** in a 1:2 ratio.

4.1.2. Method (b)

To a solution of **2** (0.100 g, 0.203 mmol) in CH_2Cl_2 (15 ml) was added acetamide (0.012 g, 0.203 mmol). The solution was stirred for 30 min before it was filtered. The solvent was evaporated under reduced pressure to leave a beige powder, which was washed with pentane (10 ml) and diethyl ether (10 ml) and dried under vacuum (0.090 g, 87% yield). Yellow crystals suitable for X-ray diffraction were obtained by recrystallisation from CH_2Cl_2/pentane.

4.1.3. Spectroscopic data for 6

IR (CH_2Cl_2) ν (cm^{-1}): 1654, 1612 (C=O); ^1H NMR (CD_2Cl_2): δ = 0.86 (d, $^1J_{PH}$ = 2.1 Hz, 3H, Pd–Me), 2.32 and 2.34 (two s, 6H, C(O)CH_3), 6.15 and 6.35 (br s, 2H, NH_2), 9.12 (br s, 1H, NH); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = –0.1 (s, Pd–Me), 23.9 (s, NHC(O)CH_3), 27.2 (s, $NH_2C(O)CH_3$), 183.4 (d, $^{2+3}J_{PC}$ = 4.3 Hz, NHC(O)CH_3), 184.1 (d, $^4J_{PC}$ = 1.9 Hz, $NH_2C(O)CH_3$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 80.3. $C_{17}H_{22}BF_4N_2O_2PPd$: calculated C, 39.99; H, 4.34; N, 5.49; found: C, 40.02; H, 4.23; N, 5.23%.

4.2. X-ray crystallographic analysis

The relevant data for **6**·0.5 CH_2Cl_2 are summarised in Table 2 [18,19]. Data were recorded on a KappaCCD diffractometer, at 173 K, using a Mo-Kα graphite monochromated radiation of 0.71073 Å. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions with isotropic thermal parameters. Fig. 3 was generated using ATOMS 5.0.7 and Fig. 3 was created with CrystalMaker 4.0.

Table 2. X-ray experimental data for **6**·0.5 CH_2Cl_2.

Formula	$C_{35}H_{46}B_2Cl_2F_8N_4O_4P_2Pd_2$
Molecular weight	1106.01
Color	colorless
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	13.046(2)
b (Å)	12.817(2)
c (Å)	13.805(2)
β (°)	95.002(3)
V (Å^3)	2299.4(7)
Z	2
Crystal dim (mm)	0.20 × 0.20 × 0.20
ϱ (calcd) (g cm^{-3})	1.597
F(000)	1108
μ (mm^{-1})	1.040
Temperature (K)	173
Reflections collected	6855
Reflections with $I > 2\,\sigma(I)$	5843
$R(gt)$[a]	0.042
Rw[a]	0.111
Goodness of fit	1.047

[a] Determined for reflections greater than threshold.

. Supplementary material

The crystallographic material has been sent to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, as supplementary material CCDC 166432 and can be obtained by contacting the CCDC (quoting the article details and the corresponding SUP number). See http://www.rsc.org/suppdata/166432 for crystallographic files in .cif format.

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