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Note

Unexpected orthopalladation of acetophenonephenylhydrazone

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Abstract

A singular hydrazonato complex of palladium has induced the unexpected *ortho* metallation of acetophenonephenylhydrazone on the phenyl group. This is the first X-ray characterized example of an *ortho* palladated *E*-arylhydrazone of general formula ArC(R'') = N-NHAr' where the metallated aryl is Ar' although palladation on Ar is not hindered. Structural evidence suggests that the Pd-N(amido) bond that is present in the starting material induced the palladation of the unexpected phenyl. \bigcirc 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Organometallic complexes of palladium are a group of chemicals of great interest as deduced from the huge number of references and books devoted to this subject. Particular attention is centered in their applications to organic synthesis [1]. Palladation reactions have been widely studied, and N-donor ligands capable of giving metallacycles have been thoroughly explored during the last decades and more recently with regard to the synthesis, reactivity, structural and mechanistic aspects [2–4]. Most of the N-donor ligands, like amines, imines and azobenzenes are limited to C-H activation and, in these cases, the products of their palladation reaction can be quite precisely anticipated. However, the task become less easy when the ligands have two or more distinct C-H bonds to activate or, even more, when they have competitive N-H bonds to deprotonate. This is the case of arylhydrazone ligands ArC(R'')=NNHAr', where Ar (the C-bonded aryl group) and Ar' (the Nbonded aryl group) represent differently substituted (R or R') phenyl groups. As ortho palladation can occur on each aryl and Z or E forms can be adopted by

* Corresponding author *E-mail address:* gherbosa@ubu.es (G. García-Herbosa). hydrazone ligands, four different *ortho* palladation modes can be predicted for arylketones and arylaldehides of arylhydrazones (see Scheme 1).

Whereas structures with Ar *ortho* palladated (E) and with Ar' ortho palladated (Z) have been reported, no examples of Ar orthopalladated (Z) and of Ar' orthopalladated (E) have been described at the moment. When the iminic nitrogen further coordinates to palladium, the palladacycle thus formed has been denominated endo (the C=N bond inside the palladacycle) or exo (the C=N bond outside the palladacycle) [5]. In that work, the use of a large variety of substituted benzilidenearylhydrazones allowed isolation and ¹H NMR characterization of examples with endo and exo coordination modes. For the Ar ortho palladated cases, the arylhydrazone adopted the E form, the only allowing endo cyclopalladation. On the contrary, the Z isomeric form was reported to be adopted by all the Ar' cyclopalladated cases, although both forms E and Zwere able to undergo exo cyclopalladation. Sterical reasons were used to explain this preference. Although not in a large extent, metallation on the Ar' group was reported to be more stable than on Ar for ArC(H) =NNHAr'. However, in the two X-ray structurally characterized examples, the Ar group is 2,4,6-trimethylphenyl, obviously unable to ortho metallate [5]. A search

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for palladated complexes of arylhydrazones in the Cambridge Crystallographic Data Base shows that acetophenonephenylhydrazone always appears metallated or cyclometallated at the Ar, i.e. at the C-bonded phenyl group and under the *E* form [6-9]. No one crystal structure appeared palladated on the Ar' (the Nbonded aryl) group when the Ar (the C-bonded aryl) group is able to *ortho* palladate.

Another important feature of arylhydrazones, ArC(R)=NNHAr', is their possibility to activate the N-H bond giving hydrazonato complexes. Examples of palladium amido complexes of acetophenonephenylhydrazone showing both N-H and C-H (at the C-bonded Ar group) deprotonated bonds have been reported [8,9]. The importance of the N-H bond to facilitate or not the *ortho* palladation of the N-bonded aryl group has been also pointed out [10].

2. Experimental

2.1. Instrumentation

¹H NMR spectra were recorded on a Bruker AC 80 instrument. ¹³C NMR was recorded on a Bruker 200 instrument. ¹H chemical shifts were measured with TMS as internal reference. ¹³C chemical shifts were measured with reference to the residual solvent resonances. IR spectra were recorded as KBr disk on a Nicolet Impact 410 instrument. Microanalyses were performed by the SCAI (Servicio Central de Apoyo a la Investigación) de la Universidad de Burgos.

2.2. Reagents and materials

PPh₃ was obtained from Aldrich Química S.A. Complexes $[Pd{C_6H_4C(Me)=N-NHPh}(\mu-Cl)]_2$ [15] and $[Bu_4N][Pd{C_6H_4C(Me)=N-NHPh}{N(Ph)-N=}C(Me)C_6H_4}(\mu-Cl)PdCl]$ [11] were prepared by published procedures. All reactions were carried out using Schlenk techniques under nitrogen atmosphere. Solvents were distilled and dried over calcium dihydride (hexane and methylene chloride) or drierite (acetone), and degassed by standard methods prior to use.

2.2.1. Preparation of trans- $[PdCl(PPh_3)_2 \{C_6H_4NH-N=C(Me)Ph\}] \cdot 0.5(Me)_2CO(1)$

 $[Bu_4N][Pd\{C_6H_4C(Me)=N-NHPh\}\{N(Ph)-N=$ $C(Me)C_6H_4$ {(µ-Cl)PdCl] (100 mg, 0.1 mmol) was dissolved in acetone (50 ml) and PPh₃ (104 mg, 0.4 mmol) was added to the red solution. The mixture was refluxed under nitrogen atmosphere for 6 h. Under these conditions, a yellow solid appeared; this was isolated by filtration, washed with acetone and dried in vacuo (10 mg, 0.011 mmol, 11%). Characterization data are as follows. Anal. Calc. for $PdC_{51.5}H_{46}N_2P_2ClO_{0.5}$ ($M_r =$ 904.75): C, 68.37; H, 5.12; N, 3.10. Found: C, 68.22; H, 4.97; N, 3.13%. ¹H NMR (CDCl₃): δ 2.04 (s, 3H, CH₃COCH₃), 2.15 (s, 3H, CH₃), 5.93 (m, 1H, agostic aromatic), 6.57 (m, 3H, aromatics), 7.37 (m, 35H, aromatics), 8.02 (s, 1H, NH). ${}^{13}C{}^{1}H, {}^{31}P{}$ (CDCl₃): δ 206.36 (C=O), 146.55, 139.71, 137.67, 134.75 (PPh₃), 134.67 (PPh₃), 134.58, 131.14, 130.83 (agostic C), 130.53 (PPh₃), 130.17 (PPh₃) 128.29, 128.23 (PPh₃), 128.16 (PPh₃), 128.09, 127.29, 125.30, 123.92, 119.79, 114.03, 28.2 (CH_3COCH_3), 11.68 (CH_3). IR: 3293 cm⁻¹ (vNH), 1711 cm⁻¹ (vC=O), 1571 cm⁻¹ (vC=N).

2.2.2. Preparation of trans-

 $[PdCl(PPh_3)_2 \{C_6H_4C(Me) = N-NHPh\}] (2)$

To a stirred suspension of $[Pd{C_6H_4C(Me)=N-$ NHPh $\{(\mu-Cl)\}_2$ (100 mg, 0.14 mmol) in methylene chloride (50 ml) under nitrogen atmosphere was added PPh₃ (73 mg, 0.28 mmol). In 30 min, the complex dissolved to give a yellow solution. After stirring for 2 h, the solution was filtered through kieselgur to remove any trace of solid and the solvent was removed in vacuo to saturation. An excess of hexane (25 ml) was added. Under these conditions, a yellow solid appeared; this was isolated by filtration, washed with hexane (2×15) ml), crystallized from methylene chloride-hexane and dried in vacuo to provide 192 mg (0.22 mmol, 85%) of the complex 2. Characterization data are as follows. Anal. Calc. for $PdC_{50}H_{43}N_2P_2Cl$ ($M_r = 875.71$): C, 68.58; H, 4.95; N, 3.20. Found: C, 68.32; H, 4.76; N, 3.11%. ¹H NMR (CDCl₃): δ 2.35 (s, 3H, Me), 6.58 (m, 2H, aromatics), 7.06 (m, 4H, aromatics), 7.52 (m, 33H, aromatics), 9.11 (s, 1H, NH). IR: 3197 cm⁻¹ (vNH), 1598 cm⁻¹ (ν C=N).

2.3. X-ray diffraction study of 1

Crystals were grown from methylene chloride-hexane. Data were collected on a Enraf-Nonius CAD4 diffractometer. The structure was solved by Patterson methods, phase expansion, and subsequent Fourier maps with DIRDIF [20]. Full-matrix least-squares refinement was made with SHELX-93 [21]. After anisotropic refinement, several peaks were found near the inversion center. These were identified as corresponding to a molecule of acetone which was refined as a rigid model with occupancy = 0.5 (this being consistent with analytical and ¹H NMR data). Perspective drawing in Fig. 1 was made with PLATON [22]. $C_{50}H_{43}ClN_2P_2Pd\cdot 0.5$ Me₂CO, M = 904.74, triclinic, space group $P\overline{1}$, a =9.671(6) Å, b = 11.278(3) Å, c = 21.38(3) Å, $\alpha =$ $81.31(4)^\circ$, $\beta = 80.26(3)^\circ$, $\gamma = 74.66(4)^\circ$, V = 2203(4) Å³, Z = 2, $D_{calc} = 1.36$ mg m⁻³, crystal size $0.24 \times 0.20 \times 0.18$ mm³, F(000) = 900, T = 293(2) K, Mo K α radiation, $\lambda = 0.71073$ Å. Also 8737 reflections were collected, giving 8616 independent reflections after merging $(R_{\text{int}} = 0.0437)$, with 6858 reflections having $I > 2\sigma(I)$. The Θ range for data collection was from 0.97 to 26.01°. The final indices $[I > 2\sigma(I)]$ were $R_1 = 0.0532$, $wR_2 =$ 0.1399.



Fig. 1. Perspective view of the molecule of **1**, showing the atom numbering. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)-P(1) 2.326(2), Pd(1)-P(2) 2.338(2), Pd(1)-C(1) 2.019(4), Pd(1)-Cl(1) 2.386(16), N(1)-N(2) 1.356(5), N(2)-C(7) 1.289(6), C(2)-N(1) 1.390(6), Cl(1)-Pd(1)-P(2) 90.06(8), Cl(1)-Pd(1)-P(1) 87.37(8), P(1)-Pd(1)-C(1) 91.79(14), P(2)-Pd(1)-C(1) 90.73(14), Cl(1)-Pd(1)-C(1) 176.77(12), P(1)-Pd(1)-P(2) 177.25(4).

3. Results and discussion

Here we report the first crystal structure that shows an *E* arylhydrazone of general formula ArC(R'')=N-NHAr' *ortho* palladated on Ar', the N-bonded aryl, when both aryls are unsubstituted and plainly able to *ortho* metallate phenyls. Neither electronic nor steric effects due to substituents on the aromatic rings can be invoked to explain the preference of one phenyl over the other.

As displayed in Scheme 2, the reaction of the anionic binuclear complex $[NBu_4][Pd{C_6H_4C(Me)=N-$ NHPh}{ μ -N(Ph)-N=C(Me)C₆H₄}(μ -Cl)PdCl] [11] with an excess of triphenylphosphine afforded trans- $[PdCl(PPh_3)_2 \{C_6H_4NH - N = C(Me)Ph\}]$ (1) as yellow microcrystalline solid in low yield. Such reaction was carried out in order to test the starting complex towards reductive elimination reaction, that should lead to C-N bond formation, as can be expected for a palladium compound containing Pd-C and Pd-N(amido) bonds on a cis arrangement [12,13]. After separation of pure 1 by filtration, the mother liquors of the reaction contain a mixture of 1 and trans-[PdCl(PPh₃)₂{ $C_6H_4C(Me)=N-$ NHPh}] (2) (the isomer orthometallated on the Cbonded aryl group). The synthesis of 2, as shown on Scheme 2, has been carried out only for comparative purposes since the synthesis and structure of the related trans-[PdCl(PPh₃)₂{ $C_6H_4C(Ph)=N-NHC_6H_4-p-Cl$ }] [14] and trans-[PdCl(PEt₃)₂{ $C_6H_4C(Me)=N-NHPh$ }] [6] have been reported. Dimeric $[Pd{C_6H_4C(Me)=N-}$ NHPh $(\mu$ -Cl)]₂ [15] cleanly reacts with an excess of triphenylphosphine to afford high yield of trans- $[PdCl(PPh_3)_2 \{C_6H_4C(Me)=N-NHPh\}]$ (2). Formation of 1 from the precursor amido complex requires a proton and the source of H^+ is unknown. It surely accounts for the low observed yield. From these results it is clear that the unexpected activation of the Nbonded phenyl group has been very likely promoted by



Scheme 2.

the previous deprotonation of one of the N–H bonds leading to formation of a Pd–N(amido) bond. The observed stability of both isomers, **1** and **2**, indicates that formation of each one is not a matter of thermodynamic but kinetic reasons. We only have to find the right pathway to build the desired chemical bond. In this case, the palladation of the N-bonded phenyl ring has been achieved even starting from the acetophenonephenylhydrazone palladated in the C-bonded phenyl group. It means that the Pd–N(amido) bond has induced special reactivity on the N-bonded phenyl ring that, finally, *ortho* metallates.

The ¹H NMR spectrum of **1** shows a singlet at 8.02 ppm due to the proton of the N–H group whereas for complex **2** it appears at 9.11 ppm. Although it is well known that the chemical shift for protons belonging to N–H groups is strongly dependent on the solvent, the observed shift to highfields for **1** can be assigned in this case to the relatively short distance $H \cdots Pd$ as discussed below. The multiplet at 5.93 ppm is assigned to the proton attached to C(6)—see Fig. 1—and involved on an weak agostic $Pd \cdots H-C$ interaction.

The IR spectrum of 1 shows the C=N band at 1571 cm^{-1} and N-H at 3293 cm^{-1} . The IR spectrum of 2 shows the C=N band at 1598 cm^{-1} and N-H at 3197 cm^{-1} .

A thermal ellipsoid drawing of **1** is provided in Fig. 1.

Complex 1 shows square planar coordination. The largest deviation from the mean plane determined by the five atoms Pd(1)-P(1)-P(2)-Cl(1)-C(1) is 0.032(1) Å and affects to Pd(1). Another plane in the complex is that defined by the ten atoms Pd(1)-C(1) to C(6)-C(7)-N(1)-N(2) where the largest deviation from the mean plane, which affects to C(7), is 0.043(4) Å. Both planes are almost perpendicular with an angle of $88.8(1)^{\circ}$.

Two agostic $Pd\cdots H$ interactions emerge from the analysis of the structure. One involving $Pd\cdots H-C(6)$ which shows a calculated parameter $r_{bp} = 1.62$ Å. The other one involves $Pd\cdots H-N(1)$ and the calculated r_{bp} is 1.5 Å. Both values are in the range of weak agostic interactions [16].

In complex 1, the hydrazone shows the *E* form (both aryl groups are *trans* with regard to the C=N double bond), the same form found in the amido precursor and in all complexes shown in Scheme 2. Although the *E* form is the commonly found for metallated arylhydrazones [6-9,14] the *Z* form has been that chosen by those arylhydrazones palladated on the N-bonded aryl Ar' mentioned above [5]. Thus complex 1 is, to the best of our knowledge, the first X-ray characterized case where an arylhydrazone (*E*) has been palladated on the N-bonded aryl Ar'. As shown in Scheme 3, two structural possibilities (rotational conformers A and B) can be anticipated for the acetophenonephenylhydrazone (*E* isomer) palladated on the N(bonded) aryl. Disposition B, which allows for Pd···N(imino) interaction is actu-





ally avoided. Disposition A, which strains Pd···H interaction, is that found. This behavior suggests an interesting question: what is hindering the Pd. N(iimino) interaction avoiding a five member palladacycle? One answer is that palladium (II) is not prone to pentacoordination as it has been found for the complex to 2, trans-[PdCl(PEt₃)₂{ $C_6H_4C(Me)=N$ similar NHPh}], where the imino nitrogen lies far from palladium (4.260 Å) avoiding repulsive interaction between the filled $4d_{z2}$ -orbital and the lone pair on the imino nitrogen [6]. Our answer is that the structure found is that which prevents approaching of the other phenyl ring to palladium that could lead to a tridentate $C^{\wedge}N^{\wedge}C$ dicyclopalladated acetophenonephenylhydrazone whose structural formula is shown in Scheme 3. Such structure has not been reported so far and its absence is consistent with the transphobia effect reported for palladium, according to which, arylpalladium complexes show preference to coordinate hard ligands in position *trans* to the Pd-C(aryl) bond [17,18]. We have not found in the Structural Data Base of Cambridge any structure of a ligand containing the two trans dicyclopalladated aryl groups on such tridentate C^NC fashion. In fact this is uncommon for any metal. The synthesis and structural characterization of platinum complexes with 2,6-diphenylpyridine acting as tridentate $C^{N}C$ ligand has been reported recently [19], but it has been pointed out that the behavior of palladium and platinum towards tridentate ligands can be divergent leading to very different results [4]. This does not mean that the dipalladated complex shown in Scheme 3 cannot exist. It just means that kinetic barriers are very important and that the right pathway leading to its formation has not yet been discovered, this representing an interesting synthetic challenge.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-166143. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: depositccdc.cam.ac.uk).

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