Synthesis and Structure of an Asymmetric Binuclear Phenylhydrazonato Anionic Complex of Palladium Containing a Pd−C(aryl) Bond *cis* to a Pd−N(amido) Bond

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Dedicated to Professor D. Rafael Uson on the occasion of his 75th birthday

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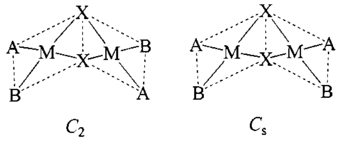
The synthesis and structure of a unique asymmetric folded binuclear anionic complex of palladium containing two different hydrazonato ligands and showing a Pd–N(amido) bond *cis* to a Pd–C(aryl) bond is described.

Introduction

Organometallic complexes of the platinum-group metals containing M−N(amido) bonds arranged *cis* to the M−C bond are of interest for their role as catalysts in important reactions that involve C−N bond formation, such as alkene hydroamination[1,2] and the synthesis of arylamines from aryl halides,[3] or in other processes such as hydrogenation of imines.[4,5] Non-planar binuclear complexes formed by two equivalent square-planar halves can exhibit C_2 or C_s symmetry (see Scheme 1 where M means any metal with square-planar geometry, X any atom or group of atoms bridging the two equivalent sides and A and B are different ligands). The most commonly found C_2 isomers are chiral even when formed by two equivalent moieties.



Scheme 1

Arylhydrazones are versatile ligands that provide both C−H and N−H bonds to activate. Binuclear orthopalladated phenylhydrazonato C_2 palladium(II) complexes containing Pd−C(aryl) bonds arranged *trans* to terminal Pd−N(amido) bonds have been reported, thus proving that, although rare, it is possible to obtain palladium compounds containing both bonds.[6,7] Mononuclear complexes of general formula $[PdAr(NHPh)(PMe_3)_2]$ with these two bonds in *trans* array have also been reported.[8] They were stabilized against the natural tendency of terminal Pd−N(amido) bonds to make bridges, by using P-donor ligands *cis* to the amido bond.

The stabilization of palladium compounds containing Pd−C and Pd−N(amido) bonds in a *cis* disposition has been achieved introducing the P-donor nonlabile chelating ancillary ligand DPPF [1,1′-bis(diphenylphosphanyl)ferrocene].[3] An interesting example is the recently reported mononuclear palladium hydrazonato complex $[Pd(DPPF)(Ar)(NH{-}N{=}CPh_2)]$ (Ar = *p*-tolyl); it undergoes C−N reductive elimination and plays and active role in the catalytic arylation of diphenylhydrazones.[9]

Results and Discussion

Here we report the synthesis and structural characterization of $[Bu_4N][Pd\{C_6H_4C(CH_3){=}N{-}NHPh\}\{\mu\text{-}N(Ph){-}N{=}C(CH_3)C_6H_4\}(\mu\text{-}Cl)PdCl]$ (**1**), an asymmetric C_1 binuclear phenylhydrazonato palladium(II) complex containing a Pd−C(aryl) bond *cis* to a Pd−N(amido) bond. It is a remarkable structure since binuclear complexes have commonly two equivalent halves and also because the *cis* arrangement of amido and aryl bonds around the palladium center is achieved without the use of P-donor ligands.

The reaction of the dimeric orthopalladated complex $[Pd\{C_6H_4C(CH_3){=}N{-}NHPh\}(\mu\text{-}Cl)]_2$[10] with Bu_4NOH (molar ratio 1:1) in MeOH cleanly affords **1** in 79% yield. The use of an excess of Bu_4NOH (molar ratio 1:2) led to the same result indicating that the second N−H bond is difficult to deprotonate. The ^1H NMR spectrum of **1** shows two sharp singlets at δ = 2.18 and 2.24 corresponding to two methyl groups, demonstrating the presence of two non-equivalent hydrazonato ligands. A multiplet at δ = 6.28 is

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assigned to the proton attached to C(14) and involved in a weak agostic Pd(2)−H−C(14) interaction.[11] The IR spectrum of **1** shows two C=N bands at $\tilde{\nu}$ = 1574 and 1587 cm^{-1}.

An ORTEP drawing of **1** is provided in Figure 1. The two previous examples of binuclear palladium hydrazonato complexes found in the Cambridge Crystallographic Database correspond to species with two equivalent halves and the Pd−C(aryl) bond *trans* to the Pd−N(amido) bond.[6,7] No previous examples of binuclear palladium(II) complexes containing a Pd−C bond *cis* to a Pd−N(amido) bond were found. Complex **1** consists of two square-planar units in a folded (C_1) array bridged by one chlorine atom and one hydrazonato ligand. The folding angle between the two coordination planes is 133.72(1)°. While both phenylhydrazonato ligands present in **1** are orthometallated to each palladium atom in a five-membered well-known fashion, only one phenylhydrazonato ligand is *N*-deprotonated. Thus, one of the phenylhydrazonato ligands is doubly deprotonated, at the C−H bond of the phenyl group and at the N−H bond. The other phenylhydrazonato ligand is singly deprotonated at a C−H bond of the phenyl group keeping the NH group protonated and uncoordinated. Attention has recently been paid to metal complexes containing a pendant NH group that can be considered as being in the intermediate coordination sphere, as they are neither directly bound to the metal center nor being in the outer sphere.[12] It allows selective two-point binding of other ligands such as ketones that may bond normally to the metal center and through hydrogen bond interaction to the NH group.

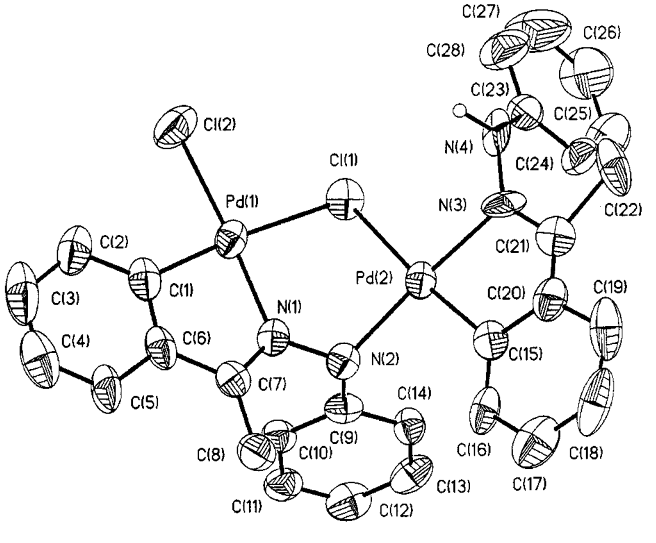
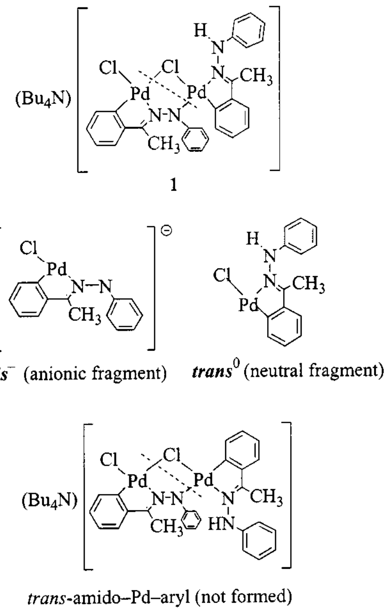


Figure 1. ORTEP drawing of **1**; hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: Pd1−Pd2 3.533(1), Pd1−C1 2.008(17), Pd1−N1 2.084(12), Pd1−Cl1 2.434(5), Pd1−Cl2 2.310(6), Pd2−C15 1.99(2), Pd2−N2 2.021(16), Pd2−N3 2.052(17), Pd2−Cl1 2.412(5), N1−N2 1.42(2), N3−N4 1.36(3); Cl2−Pd1−C1 94.0(9), C1−Pd1−N1 81.6(9), N1−Pd1−Cl1 92.8(5), Cl1−Pd1−Cl2 91.5(2), Cl1−Pd2−N2 89.3(5), N2−Pd2−C15 95.9(9), C15−Pd2−N3 79.0(9), N3−Pd2−Cl 95.9(5)

The sum of the four angles is 359.9° for Pd(1) and 360° for Pd(2). The Pd(2)−N(2) amido distance is 2.021(16) Å, similar to 2.035(9) Å which is the distance found in $[Pd(DPPF)(Ar)(NH{-}N{=}CPh_2)]$[9], a complex containing also a Pd−C(aryl) bond *cis* to a Pd−N(amido) bond. The N−N distance is noticeably different in both hydrazonato ligands. In the bridging one the N(1)−N(2) bond length is 1.42(2) Å, whereas in the other one the corresponding N(3)−N(4) distance is 1.36(3) Å. They are extreme examples of the typical N−N bond-length range in hydrazones (1.38−1.41 Å).[13]

A detailed discussion of the mechanism leading to **1** is not possible at this stage. In any case, it is clear that complex **1** is the result of the coupling of two monometallic fragments through the dashed line as shown in Scheme 2.



Scheme 2

The final geometry requires that the fragment containing the deprotonated nitrogen atom has a *cis* configuration of C and Cl atoms, whereas the fragment with the protonated nitrogen must bear a *trans* arrangement of Cl and C. It is likely that the reaction involves the cleavage of the symmetric parent dimer, probably by incorporation of solvent molecules (methanol) as labile ligands. Quantum chemical calculations using the PM3 model implemented in MacSpartan Pro indicate that for the neutral fragment the *trans* "C−Pd−Cl" array is more stable than the *cis* one by 4.174 $kcal{\cdot}mol^{-1}$. On the contrary, for the anionic fragment the *cis* arrangement is more stable than the *trans* one by 5.635 $kcal{\cdot}mol^{-1}$, this being consistent with the formation of the resulting geometry. Additionally, calculations carried out on both **1** and its *trans* amido−Pd−aryl isomer (see Scheme 2) indicate that the *cis* isomer **1** is more stable than the alternative *trans* isomer by ca. 18 $kcal{\cdot}mol^{-1}$. Arylpalladium complexes tend to coordinate hard ligands in a position *trans* to the Pd−C(aryl) bond and to avoid coordination of soft ligands. This fact has been reported as transphobia,[14,15] and is followed in *trans*-$[PdAr(NHPh)(PMe_3)_2]$.[8] In complex **1** the hard N(amido) ligand arranges *cis* to the Pd−C(aryl) bond, leaving the softer ligand chloro in *trans* position to the Pd−C(aryl) bond. The alternative *trans* isomer of **1** would contain a Pd−C(aryl) bond with the harder amido ligand in *trans* position, obeing transphobia arguments, but this isomer is not formed. Further, but elusive at the moment, examples of amido−palladium−aryl complexes seems to be required to be able to say more about the factors that control the arrangement of these C and N donor ligands around the palladium center.

Interestingly, in spite of the adequate (and unusual) *cis* arrangement of the aryl and amido ligands to undergo reductive elimination reaction, complex **1** showed to be very stable when heated under reflux in acetone. Even in excess of PPh_3 the products of the reaction do not contain Pd^0 but Pd^{II} derivatives whose characterization is currently being carried out.

Experimental Section

General: ^1H (80 MHz) and ^{13}C (200 MHz) NMR data were collected in $CDCl_3$ solutions (298 K) using TMS as standard reference with a Bruker AC 80 and with a Varian VXR 200 spectrometer, respectively. Elemental analyses were performed by the Servicio Central de Apoyo a la Investigación of the University of Burgos (Spain).

Preparation of $[Bu_4N][Pd\{C_6H_4C(CH_3){=}N{-}NHPh\}\{\mu\text{-}N(Ph){-}N{=}C(CH_3)C_6H_4\}(\mu\text{-}Cl)PdCl]$ (1): 200 mg (0.28 mmol) of $[Pd\{C_6H_4C(CH_3){=}N{-}NHPh\}(\mu\text{-}Cl)]_2$[10] were suspended in 50 mL of dichloromethane, and then 0.28 mL (0.28 mmol) of Bu_4NOH (1 M solution in methanol) was added. After stirring for 30 min at room temperature, the complex was completely dissolved to afford a red solution. The solution was stirred for 6 h and then it was filtered through kieselgur in order to remove any traces of solid. The filtrate was concentrated in vacuo and layering with hexane afforded a red precipitate which was collected and washed with hexane. The product was recrystallised from dichloromethane/hexane to yield 206 mg (79%) of the complex **1**. − $C_{44}H_{61}Cl_2N_5Pd_2$: calcd. C 55.99, H 6.52, N 7.42; found C 55.62, H 6.42, N 7.15. − ^1H NMR: δ = 0.91 [m, 12 H, $(^{\delta}CH_3)_4N-$], 1.32 [m, 16 H, $(-^{\gamma}CH_2-^{\beta}CH_2)_4N-$], 2.18 [s, 3 H, $-C(CH_3){=}N{-}N{-}Ph$], 2.24 [s, 3 H, $-C(CH_3){=}N{-}N(H){-}Ph$], 3.13 [m, 8 H, $(-^{\alpha}CH_2)_4N$], 6.28 (m, 1 H, agostic), 6.99 (m, 14 H, aromatic), 7.65 (m, 2 H, aromatic), 7.91 (m, 1 H aromatic), 8.98 (s, 1 H, −NH−). − $^{13}C\{^1H\}$ NMR: δ = 13.8, 14.1, 14.2, 19.8, 24.0, 58.5, 113.0, 114.6, 115.6, 121.7, 123.0, 123.6, 124.5, 125.2, 125.6, 126.4, 127.7, 128.4, 128.6, 129.0, 130.2, 135.1, 135.7, 136.4, 144.7, 146.9, 154.8, 156.0, 157.3, 158.0, 176.5, 177.2.

X-ray Crystallographic Study: Crystals of **1** were grown from dichloromethane/hexane. Data were collected with an Enraf−Nonius CAD4 diffractometer. The structure was solved by Patterson methods, phase expansion, and subsequent Fourier maps with DIRDIF.[16] Full-matrix least-squares refinement was made with SHELX-93.[17] Perspective drawing in Figure 1 was made with PLATON.[18] $C_{44}H_{61}Cl_2N_5Pd_2$, M = 944.69, monoclinic, space group $P2_1/c$, a = 21.514(4) Å, b = 20.353(4) Å, c = 20.709(4) Å, β = 86.14(3)°, V = 9048(3) Å^3, Z = 8, D_c = 1.387 Mg/m^3, crystal size 0.26 × 0.20 × 0.17 mm, $F(000)$ = 3896, T = 293(2) K, Mo-K_{α} radiation, λ = 0.71073 Å. 16378 reflections were measured, giving 8196 independent reflections after merging (R_{int} = 0.0564), with 4469 reflections having $I > 2\sigma(I)$. Two chemically equivalent but crystallographically independent anion/cation pairs were found in the asymmetric unit. The final indices $[I > 2\sigma(I)]$ were $R1$ = 0.0808, $wR2$ = 0.2074. Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-156983.Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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[1] T. E. Müller, M. Beller, *Chem. Rev.* **1998**, *98*, 675−703.

[2] H. M. Senn, P. E. Blochl, A. Togni, *J. Am. Chem. Soc.* **2000**, *122*, 4098−4107.

[3] J. F. Hartwig, *Angew. Chem. Int. Ed.* **1998**, *37*, 2046−2067.

[4] B. R. James, *Catal. Today* **1997**, *37*, 209−221.

[5] R. Dorta, P. Egli, F. Zürcher, A. Togni, *J. Am. Chem. Soc.* **1997**, *119*, 10857−10858.

[6] P. Espinet, G. García, F. J. Herrero, Y. Jeannin, M. Philoche-Levisalles, *Inorg. Chem.* **1989**, *28*, 4207−4211.

[7] P. Espinet, M. Y. Alonso, G. García-Herbosa, J. M. Ramos, Y. Jeannin, M. Philoche-Levisalles, *Inorg. Chem.* **1992**, *31*, 2501−2507.

[8] L. A. Villanueva, K. A. Abboud, J. M. Boncella, *Organometallics* **1994**, *13*, 3921−3931.

[9] J. F. Hartwig, *Angew. Chem. Int. Ed.* **1998**, 2090−2093.

[10] B. N. Cockburn, D. V. Howe, T. Keating, B. F. G. Johnson, J. Lewis, *J. Chem. Soc., Dalton Trans.* **1973**, 404−410.

[11] R. H. Crabtree, E. M. Holt, M. Lavin, S. M. Morehouse, *Inorg. Chem.* **1985**, *24*, 1986−1992.

[12] K. Gruet, R. H. Crabtree, D. H. Lee, L. Liable-Sands, A. L. Rheingold, *Organometallics* **2000**, *19*, 2228−2232.

[13] P. A. S. Smith, *Derivatives of Hydrazone and other Hydronitrogens Having N−N Bonds*, Benjamin, Reading, MA, **1983**, p.46.

[14] J. Vicente, A. Arcas, D. Bautista, P. G. Jones, *Organometallics* **1997**, *16*, 2127−2138.

[15] J. Vicente, J. A. Abad, A. D. Frankland, M. C. R. de Arellano, *Chem. Eur. J.* **1999**, *5*, 3066−3075.

[16] P. T. Beurskens, G. Admiraal, W. P. Bosman, G. Beurskens, H. M. Doesburg, S. García-Granda, R. O. Gould, J. M. M. Smits, C. Smikalla, *The DIRDIF Program System, Technical Report of the Crystallography Laboratory*, University of Nijmegen, The Netherlands, **1992**.

[17] G. M. Sheldrick, *SHELXL-93*, University of Göttingen, **1993**.

[18] A. L. Spek, *The EUCLID Package in Computational Crystallography* (Ed.: E. Sayre), Clarendon Press, Oxford, England, **1982**.

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