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[Pd(Fmes)I{NMe₂(CH₂-o-C₆H₄-I)-N,I}], a palladium(II) complex with I⁻ and organic iodide as *trans* ligands

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Dedicated to Prof. Rafael Usón, whose initiative meant more than one small step on the trail to modern Spanish Organometallic Chemistry

Abstract

The treatment of $[Pd(dmba)(Fmes)(OH_2)]$ with I₂ leads to the formation of $[Pd(Fmes)I\{NMe_2(CH_2-o-C_6H_4-I)-N,I\}]$. The X-ray structure shows that a new halocarbon ligand, (2-iodobenzyl)dimethylamine has been formed and is acting as N–I chelate. The two different types of iodine, one iodide ligand and one organic iodide coordinated to Pd, are mutually *trans* and display essentially identical Pd–I distances.

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1. Introduction

The solid state structures of main group, and of some transition metal compounds with the bulky ligand 2,4,6tris(trifluoromethyl)phenyl (nonafluoromesityl or Fmes) often show that the ortho-CF₃ groups are involved in $M \cdots F$ bonding interactions in many structures [1–3]. On the contrary, the structures of palladium(II) complexes determined so far show structural features and Pd-F distances suggestive of non interaction, which we attribute to the soft nature of Pd(II) [4]. Since the structure of the Fmes ligand places F atoms on the Pd atom and would favor geometrically this interaction, we planned to oxidize the Pd center with I_2 in the hope that the bulk iodides arising from the redox process might prefer to remain as external counteranions, while the so formed hard Pd(IV) center would achieve hexacoordination by accepting two fluorine donor atoms from the Fmes ligand (Eq. (1)). A similar strategy has worked previously for the synthesis of compounds with M-Cl(aromatic) interactions, such as in $[Pt(C_6Cl_5)_4]$ which

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has been obtained by oxidation of $(N^nBu_4)[Pt(C_6Cl_5)]$ with $Cl_2.[5]$ However it fails when applied on $[Pd(dmba)(Fmes)(OH_2)]$ (dmba = dimethylbenzylamine). In this case the Pd–C bond with the dmba ligand is split, and the new I–dmba ligand so formed remains coordinated to the Pd center.



2. Results and discussion

The reaction of $[Pd(dmba)(Fmes)(OH_2)]$ (1) with I₂ in a 1:1 molar ratio did not afford the corresponding palladium(IV) complex but led to the formation of $[Pd(Fmes)I\{NMe_2(CH_2-o-C_6H_4-I)-N,I\}]$ (2) according to Eq. (2):

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The characterization of 2 was not unequivocal from its analytical and spectroscopic data only, and its solid structure was determined by X-ray diffraction. A perspective view of one of the molecules in the asymmetric unit is shown in Fig. 1. Selected distances and angles are listed in Table 1.

Both molecules of 2 in the asymmetric unit display the same structural features. The palladium atom is approximately square planar, coordinated by a new halocarbon ligand, (2-iodobenzyl)dimethylamine, which is acting as a chelating bidentate ligand, with its iodine atom *cis* to the fluoromesityl ligand. This ligand forms with the palladium a six-membered cycle that shows a boat conformation. A iodide ligand is coordinated trans to the iodine atom, and the coordination plane is completed by a Fmes ligand. The fluoromesityl ligand lays essentially perpendicular (90.0°) to the pseudoplane defined by the metal and the donor atoms. The shortest Pd^{...}F₃C-ortho distance found in **2** is 2.987 Å (between Pd(1) and F(3), longer than those found in palladium(II) [Pd(Fmes)₂L₂] complexes, confirming that these are non bonding contacts [4].

Chelating halocarbon ligands are not uncommon and a number of structures have been reported [6,7]. However, they are observed usually when involved in the formation of particularly stable five-membered metalacycles. Only one example of a six-membered metalacycle involving a halogen as donor has been reported, in a Mo complex [8]. Obviously there are not precedents of six-membered metalacycles with a Pd–I bond. The ¹⁹F NMR spectra of **2** show a boat to boat

F(3) F(1) F(1)

Fig. 1. Molecular structure of $[Pd{NMe_2(CH_2-O-C_6H_4I)-N,I}(F-mes)I]$ (2) showing the atom numbering scheme. The elipsoids are drawn at 30% probability level.

Table 1								
Selected	bond	lengths	(Å)	and	bond	angles	(°)	for
$[Pd(Fmes)I{NMe_2(CH_2-o-C_6H_4-I)-N,I}]$ (2)								

Bond lengths			
Pd(1)-C(11)	1.93(3)	I(1) - Pd(1) - I(2)	170.40(12)
Pd(1) - N(1)	2.16(2)	C(11) - Pd(1) - N(1)	175.1(13)
Pd(1)-I(1)	2.607(3)	C(1)-I(2)-Pd(1)	91.8(9)
Pd(1)–I(2)	2.636(3)	C(7)-N(1)-Pd(1)	119.1(17)
Bond angles			
C(11) - Pd(1) - I(1)	83.4(8)	C(6)-C(7)-N(1)	112(3)
N(1) - Pd(1) - I(1)	95.1(6)	C(1)-C(6)-C(7)	121(3)
C(11) - Pd(1) - I(2)	89.4(8)	C(6) - C(1) - I(2)	120(3)
N(1)-Pd(1)-I(2)	92.6(7)	C(12)-C(11)-C(16)	112(3)

inversion of (2-iodobenzyl)dimethylamine ligand which is fast at room temperature but slow at -60 °C, as expected for a six-membered metalacycle.

The Pd(1)–I(1) distance is 2.607(3)-2.600(4) Å, remarkably similar to the Pd(1)–I(2) (2.636(3)– 2.624(4) Å) distance, in spite of the very different nature of the two iodine atoms. Moreover, both distances are similar to those found in complexes with iodide coordinated to palladium as terminal ligand [9], and to that found for Pt–I in [Pt(C₆F₅)₂{(R–I)–C,I}] (R–I = 1,2-iodoaniline) [7a]. The fact that the two iodine atoms in **2** are mutually *trans* and the metalacycle is sixmembered makes our observation of equality in distances particularly significant, as they are not affected by effects coming from different trans ligands, or by strain in a shorter cycle.

NMR experiments in CDCl₃ at low temperature were carried out in order to suggest a possible mechanism for the formation of 2, but no intermediate was detected. The clean formation of 2 suggests that the reaction might be initiated by electrophilic substitution at the easily accessible metalated carbon of the dmba, followed by coordination of the iodide and the iodocarbon, with water displacement. In such case the reaction would not involve a Pd(IV) intermediate, and the bulky iodine would not need to approach the Pd center, which is somewhat protected by the *ortho* effect of the CF₃ groups above and below the coordination plane.

Attempts at extending these results to Cl_2 or Br_2 resulted in mixtures that could not be well characterized. Considering that the chelating N,X-coordination of the 2-halodimethylbenzylamine is expected to be less favored when X is Cl, or Br (both worse donors than I), the spectroscopic data of the crude products suggest the existence of halogen bridged binuclear compounds, possibly $[Pd_2(\mu-X)_2(Fmes)_2\{NMe_2(CH_2-o-C_6H_4-X)\}_2]$ where the halocarbon ligand is coordinated only by the nitrogen. However, the mixture contains also other products revealing that the reaction is not as clean as it was for I₂.

3. Experimental

The reactions were carried out under dinitrogen atmosphere. The solvents were purified according to standard procedures [10]. [Pd(dmba)(Fmes)(OH₂)] (1) was prepared as described elsewhere [11]. Infrared spectra were recorded in Perkin–Elmer 883 or 1720X apparatuses, as Nujol mulls between polystyrene films, from 4000 to 200 cm⁻¹. NMR spectra were recorded on an ARX-300 instrument in CDCl₃, and chemical shifts are referred to TMS, or CFCl₃. Coupling constants are given in Hz. Elemental analyses were performed on a Perkin–Elmer 2400B microanalyzer.

3.1. Synthesis of [Pd(Fmes)I{NMe₂(CH₂-o-C₆H₄I)-N,I}] (**2**)

 I_2 (0.026 g, 0.1 mmol) was added to a solution of 1 (0.054 g, 0.1 mmol) in CH₂Cl₂ (10 ml). The colorless solution became deep orange instantaneously. The solution was stirred at room temperature for 2 min and then filtered on dry Celite. Hexane (ca. 30 ml) was added to the filtrate, which was concentrated, and cooled to -20 °C. The orange crystals obtained were decanted, washed with hexane $(3 \times 5 \text{ ml})$, and dried in vacuum. Yield 0.041 g (53%). ¹⁹F RMN: δ – 56.65 (br, ortho-CF₃, 6F), -63.09 (s, para-CF₃, 3F). ¹⁹F RMN $(-60 \ ^{\circ}\text{C}): \delta \ -56.61$ (s, ortho-CF₃, 3F), -56.95 (s, ortho-CF₃, 3F), -62.63 (s, para-CF₃, 3F). ¹H RMN: δ 7.79 (d, J = 8 Hz, H³, NMe₂(CH₂-o-C₆H₄I), 1H), 7.74 (s, $C_6H_2(CF_3)_3$, 2H), 7.52 (t, J = 7.5 Hz, H^5 , NMe₂(CH₂-o-C₆H₄I), 1H), 7.30 (m, NMe₂(CH₂-o-C₆H₄I), 2H), 3.69 (br, NMe₂(CH₂-o-C₆H₄I), 2H), 2.85 (br, N(CH₃)₂(CH₂-o-C₆H₄I), 6H). ¹H RMN (-60 °C): 7.79 (d, J = 8 Hz, H³, NMe₂(CH₂-o-C₆H₄I), 1H), 7.75 (s, $C_6H_2(CF_3)_3$, 2H), 7.52 (t, J = 7.5 Hz, H^5 . NMe₂(CH₂-o-C₆H₄I), 1H), 7.37 (t, J = 7.4 Hz, H⁶ NMe₂(CH₂-o-C₆ H_4 I, 1H), 7.31 (t, J = 7.8 Hz, H⁴, NMe₂(CH₂-o-C₆H₄I), 1H), 3.87 (d, J = 12.4 Hz, NMe₂(C H_2 -o-C₆H₄I), 1H),3.56 (d, J = 12.4 Hz, NMe₂(CH₂-o-C₆H₄I), 1H), 3.15 (s, N(CH₃)₂(CH₂-o- C_6H_4I , 3H), 2.53 (s, N(CH₃)₂(CH₂-o-C₆H₄I), 3H). IR: 2020 vw(br), 1868 vw(br), 1787 vw(w), 1615 m, 1568 w, 1298 vs, 1278 vs, 1180 s, 1144 s, 1082 m, 1023 m, 929 w, 914 m, 833 w, 757 m, 695 w, 683 m, 667 w, 654 d, 531 w(br), 437 w(br), 290 w(br). Anal. Calc. for C₁₈H₁₄NF₉I₂Pd: C, 27.88; H, 1.82; N, 1.81. Found: C, 28.16; H, 1.89; N, 1.71%.

4. X-ray crystallography

Suitable crystals of **2** were grown by slow diffusion of a concentrated dichloromethane solution of the complex into n-hexane at -20 °C. X-ray measurements were made using a Bruker SMART CCD area-detector dif-

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Empirical formula Formula weight	$C_{18}H_{14}F_9I_2NPd$ 775 50
Crystal system	triclinic
Space group	P Ī
$a(\dot{\Lambda})$	8 684(6)
$h(\mathbf{A})$	13 370(8)
$c(\mathbf{A})$	20.358(13)
	20.338(13)
α () β (°)	95.909(15)
p()	38.020(12)
γ () V (Å ³)	102.104(13)
V (A)	2207(2)
L D (2 cm ⁻³)	4
D_{calc} (g cm ⁻¹)	2.275
Absorption coefficient (mm)	3.021
F(000)	1448
Crystal size (mm ⁻)	$0.09 \times 0.03 \times 0.02$
1 emperature (K)	293(2)
θ range for data collection (*)	1.02 to 20.83
Wavelength (A)	0.71073 (Mo K α)
Index ranges	$-8 \le h \le 8, -13 \le k \le 13,$
	$0 \le l \le 20$
Reflections collected	8306
Independent reflections	$4693 \ (R_{\rm int} = 0.1299)$
Observed reflections $[I > 2\sigma(I)]$	1605
Absorption correction	SADABS
Max. transmission	1.000
Min. transmission	0.682
Data/restraints/parameters	4693/0/523
Goodness-of-fit on F^2	0.761
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0676, wR_2 = 0.1303$
R indices (all data)	$R_1 = 0.1890, wR_2 = 0.1661$
Largest difference Peak and hole (e	1.344 and -0.830
Á ⁻)	

fractometer with Mo K α radiation ($\lambda = 0.71073$ Å) [12]. Intensities were integrated [13] from several series of exposures, each exposure covering 0.3° in ω , and the total data set being a hemisphere. Absorption corrections were applied, based on multiple and symmetryequivalent measurements [14]. The structure was solved by direct methods and refined by least squares on weighted F^2 values for all reflections (see Table 2) [15]. All non-hydrogen atoms were refined without positional constraints and assigned anisotropic displacement parameters except for C(12), C(18), C(31), C(34), C(35), C(37), C(39) and N(2). Hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. Refinement proceeded to give residuals shown in Table 2, the poor quality of the crystal preventing a better result. Complex neutral-atom scattering factors were used [16].

5. Supporting material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 179640. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk).

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